Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

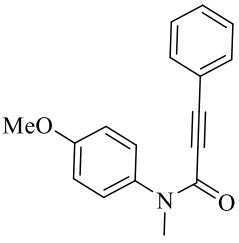
Copper(II)-Catalyzed Oxidative *ipso*-Annulation of *N*-Arylpropiolamides and Biaryl Ynones with 1,3-Diketones: Construction of Diketoalkyl Spiro-trienones

Chada Raji Reddy*, Dattahari H. Kolgave, Uprety Ajaykumar and Remya Ramesh

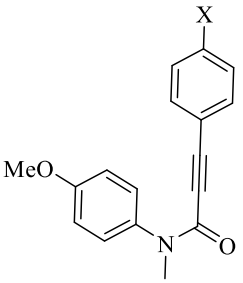
Department of Organic Synthesis & Process Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India

2. Structures of starting materials

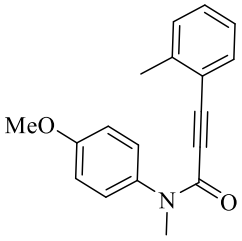
All the starting materials (**1a** to **1e**, **1g**, **1i** to **1o**)[3], (**1f**)[4], (**1h**)[1], (**4a** to **4h**)[2] and (**4i**)[5] were prepared based on literature reports, and the spectral data was compared.



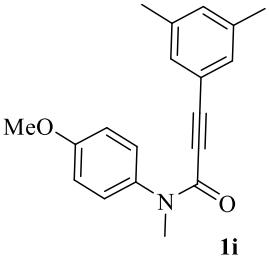
1a



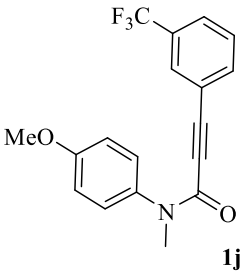
1b, X= Me,
1c, X= Cl,
1d, X= F,
1e, X= CN,
1f, X= NO_2,
1g, X= COMe



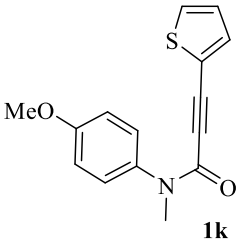
1h



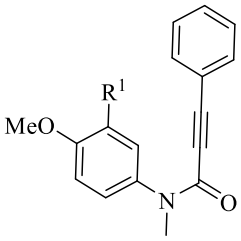
1i



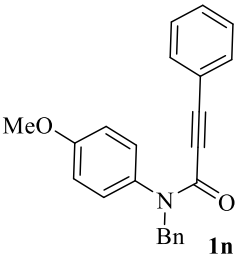
1j



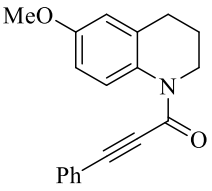
1k



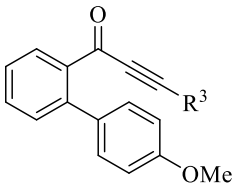
1l, R^1= Me,
1m, R^1= F



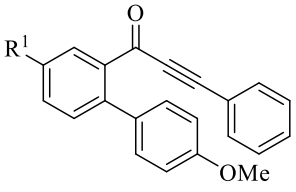
1n



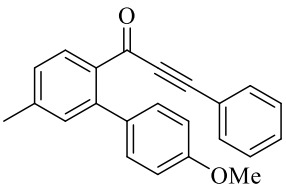
1o



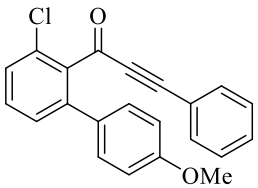
4a, R^3= Ph,
4b, R^3=Ph 4- Me,
4c, R^3= Ph 4-CN,
4d, R^3= Ph 4-CF_3



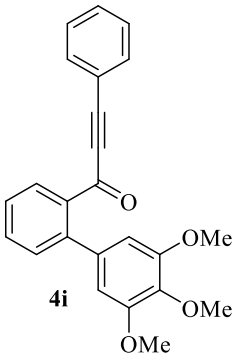
4e, R^1= F,
4f, R^1= OMe



4g



4h

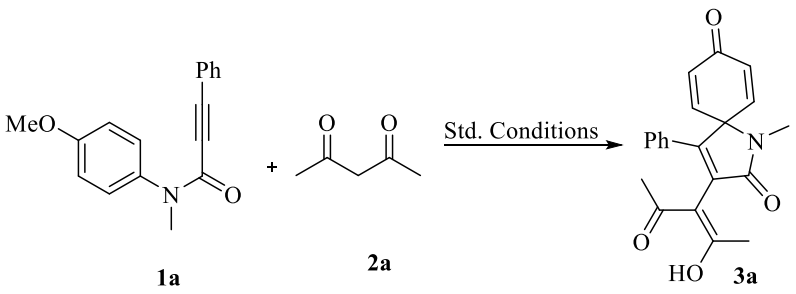


4i

3. Control experiments

Radical trapping experiment

When the Reaction of a mixture of **1a** and **2a** under the standard conditions was performed in the presence of 2.0 equiv of TEMPO, radical scavengers, **3a** was not formed.



1a **2a** **3a**

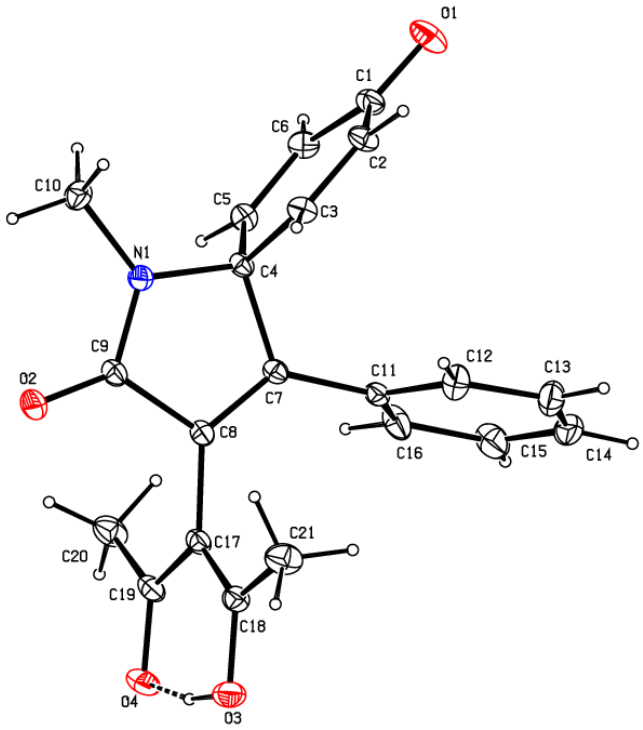
Tempo (3 equiv) **3a, 0%**

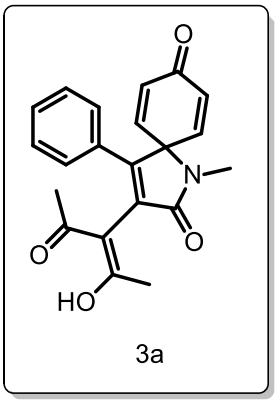
4. X-ray Crystallography.

X-ray data for the compounds **3a, 3r** and **5a** were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[6] The structure was solved using the intrinsic phasing method and further refined with the SHELXL program and expanded using Fourier techniques.[7] Anisotropic displacement parameters were included for all non-hydrogen atoms. O-bound H atom was located in the difference density map and their positions and isotropic displacement parameters were refined. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

A. Crystal structure determination of 3a

Crystal Data for $C_{21}H_{19}NO_4$ (M =349.37 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 8.7602(3) Å, b = 10.6004(3) Å, c = 10.5707(3) Å, β = 111.3688(9)°, V = 914.13(5) Å^3, Z = 2, T = 294.15 K, μ(MoKα) = 0.088 mm^{-1}, $Dcalc$ = 1.269 g/cm^3, 18725 reflections measured (4.994° ≤ 2Θ ≤ 61.186°), 5491 unique (R_{int} = 0.0724, R_{sigma} = 0.0853) which were used in all calculations. The final R_1 was 0.0534 (I > 2σ(I)) and wR_2 was 0.1511 (all data). CCDC No. 2171887 deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

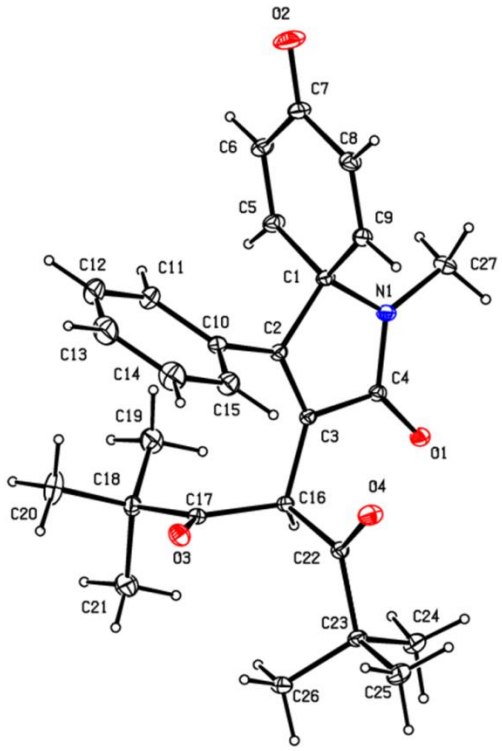


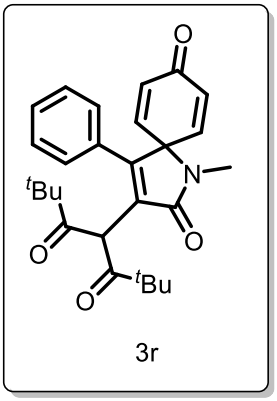


3a

B. Crystal structure determination of 3r

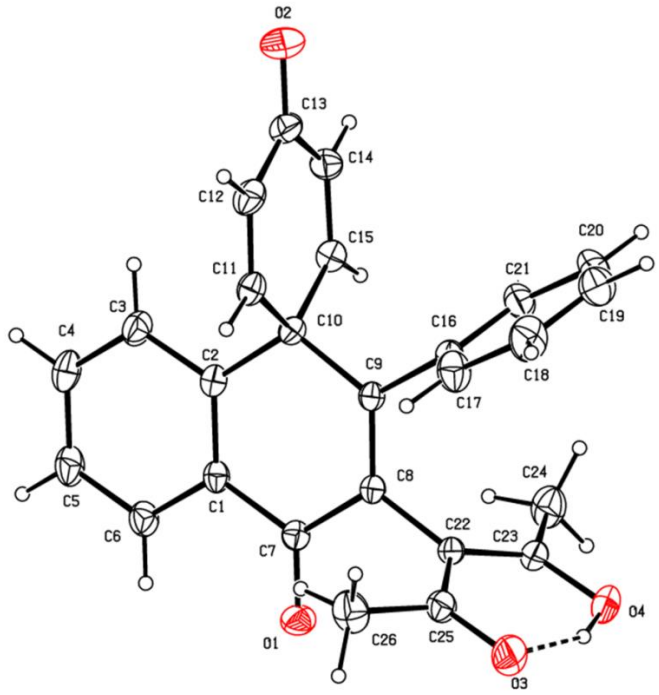
Crystal Data for $C_{27}H_{31}NO_4$ (M =433.551 g/mol): triclinic, space group P-1 (no. 2), a = 10.0686(7) Å, b = 10.3684(7) Å, c = 12.3317(8) Å, α = 72.123(2)°, β = 80.904(2)°, γ = 87.167(2)°, V = 1209.80(14) Å^3, Z = 2, T = 294.15 K, μ(Mo Kα) = 0.079 mm^{-1}, *Dcalc* = 1.190 g/cm^3, 23612 reflections measured (5.78° ≤ 2Θ ≤ 61.1°), 7363 unique (R_{int} = 0.0382, R_{sigma} = 0.0484) which were used in all calculations. The final R_1 was 0.0516 (I>=2u(I)) and wR_2 was 0.1409 (all data). CCDC No. 2171885 deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

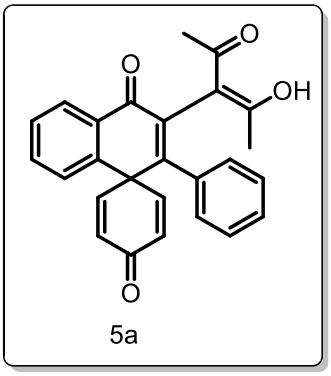




C. Crystal structure determination of 5a

Crystal Data for $C_{26}H_{20}O_4$ (M =396.42 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 18.8869(12) Å, b = 12.5379(18) Å, c = 9.037(3) Å, β = 99.986(5)°, V = 2107.7(7) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.084 mm^{-1}, *Dcalc* = 1.249 g/cm^3, 25169 reflections measured (2.19° ≤ 2Θ ≤ 61.018°), 6186 unique (R_{int} = 0.0455, R_{sigma} = 0.0570) which were used in all calculations. The final R_1 was 0.0583 (I > 2σ(I)) and wR_2 was 0.1743 (all data). CCDC No. 2171886 deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/





Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius

References:

1) Yu, K.; Kong, X.; Yang, J.; Li, G.; Xu, B.; Chen, Q. Electrochemical Oxidative Halogenation of *N*-Aryl Alkynamides for the Synthesis of Spiro[4.5]trienones *J. Org. Chem*. **2021**, *86*, 917−928.

2) Raji Reddy, C.; Kolgave, D. H. Electrochemical Selenylative Carbannulation of Biaryl Ynones to Seleno-Dibenzocycloheptenones/ Spiro[5.5]Trienones. *J. Org. Chem*. **2021**, *86*, 17071−17081.

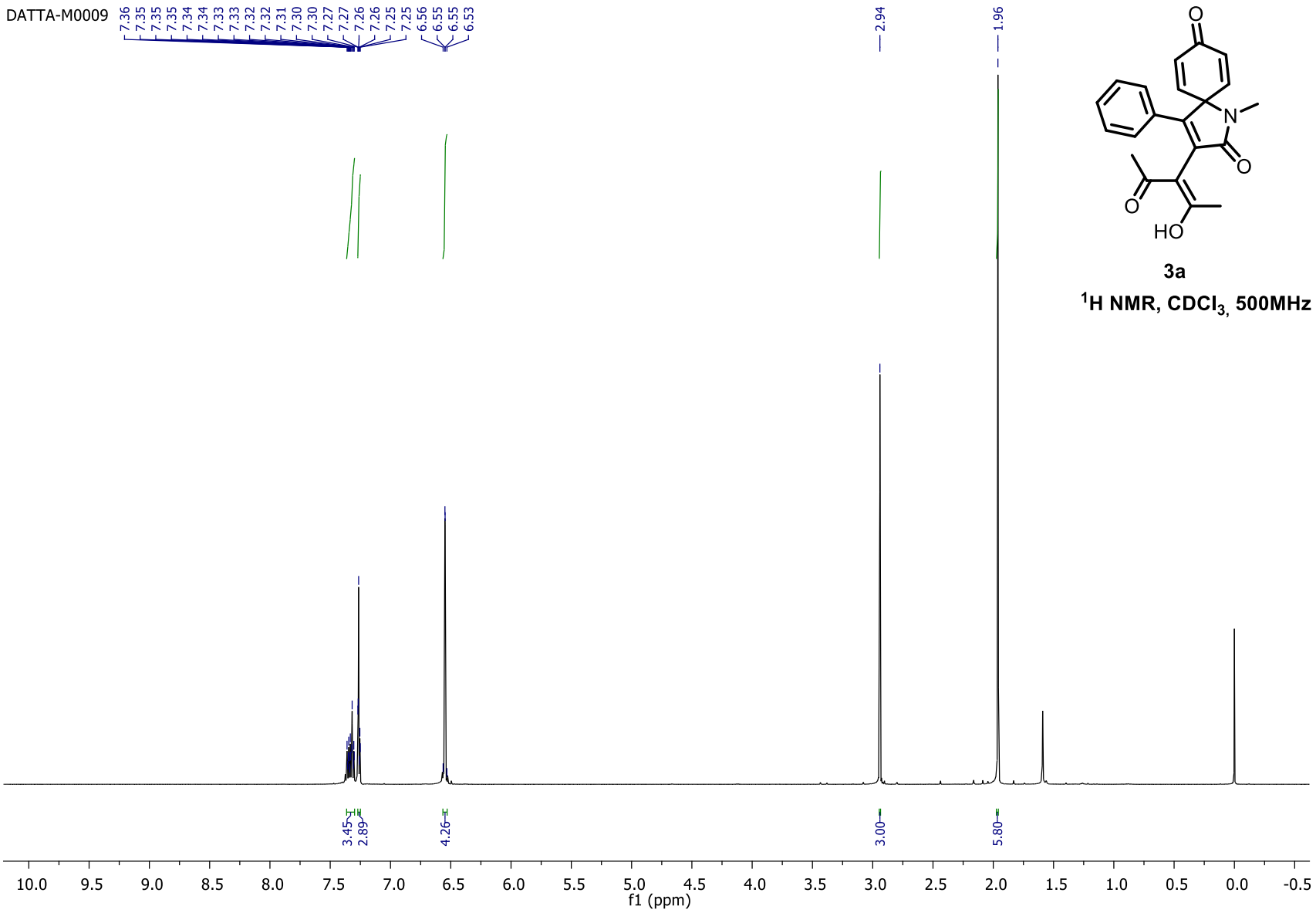
3) Raji Reddy, C.; Kolgave, D. H.; Subbarao, M.; Aila, M.; Prajapti, S. K. Ag-Catalyzed Oxidative ipso-Cyclization via Decarboxylative Acylation/Alkylation: Access to 3-Acyl/Alkyl-spiro[4.5]- trienones. *Org. Lett*. **2020**, *22*, 5342−5346.

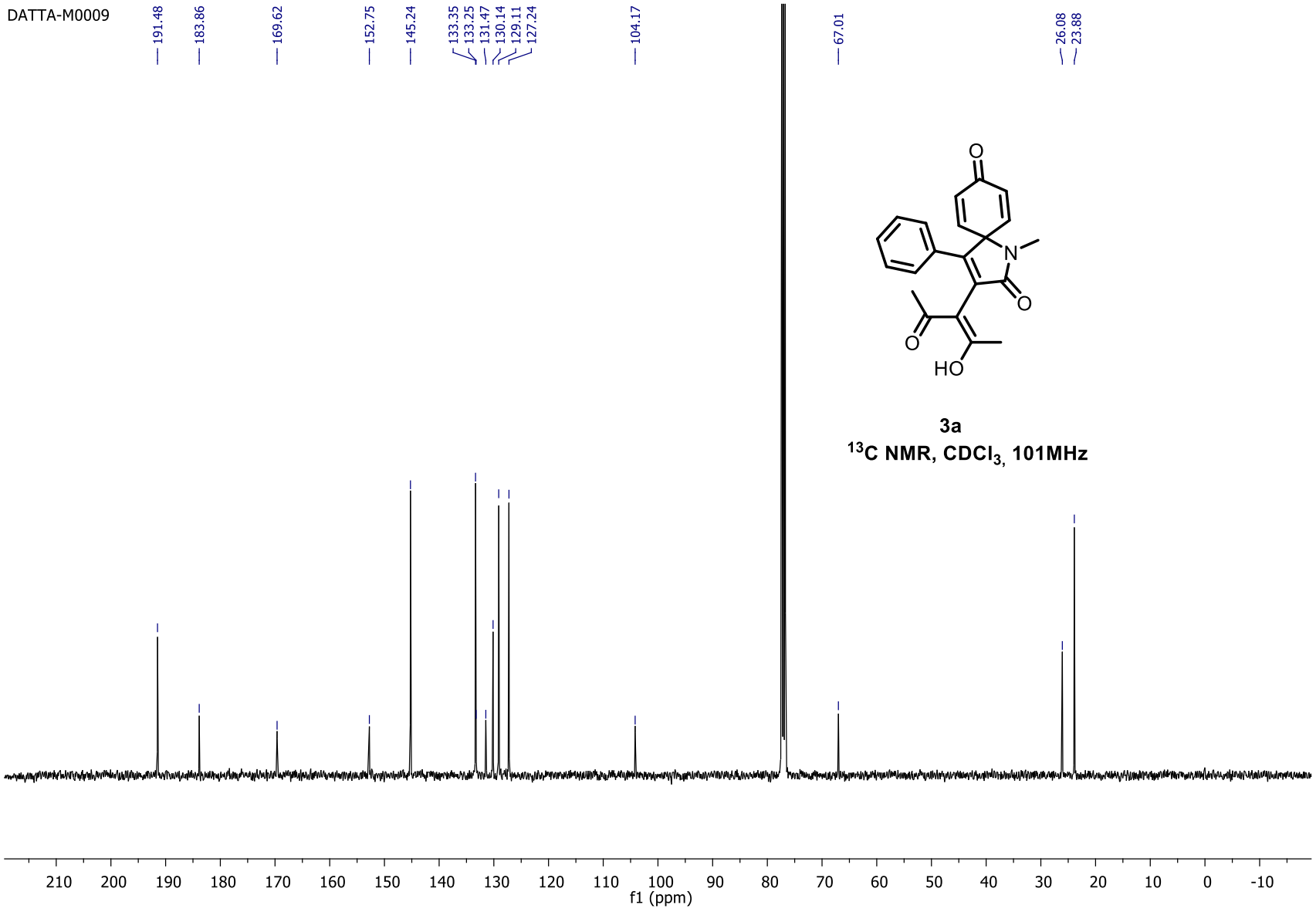
4) Raji Reddy, C.; Uprety, A.; Kolgave, D. H. Expeditious Access to Spiro-Fused 2,5-Cyclohexadienones via Thio(seleno)- cyanative ipso-Cyclization. *J. Org. Chem.* **2020**, *85*, 15521−15531.

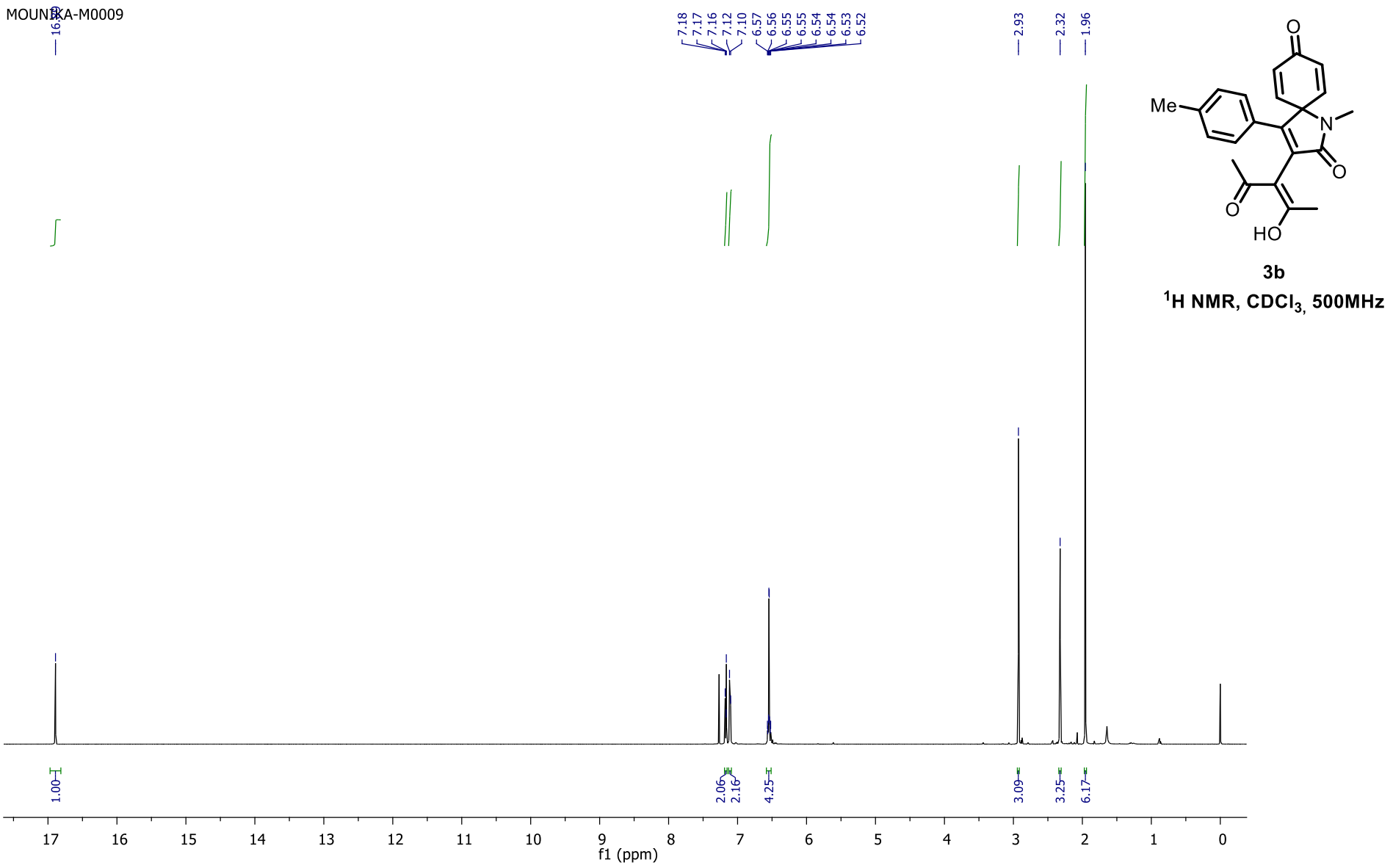
5) Zhang, M-M.; Shen, L-Y.; Dong, S.; Li, B.; Meng, F.; Si, W-J.; Yang, W-C. DTBP-Mediated Cascade Spirocyclization and Dearomatization of Biaryl Ynones: Facile Access to Spiro [5.5]trienones through C(sp^3)-H Bond Functionalization. *Eur. J. Org. Chem.* **2021**, *31*, 4465–4468.

6) Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

7) Sheldrick G. M. (2015).ActaCrystallogr C71: 3-8.

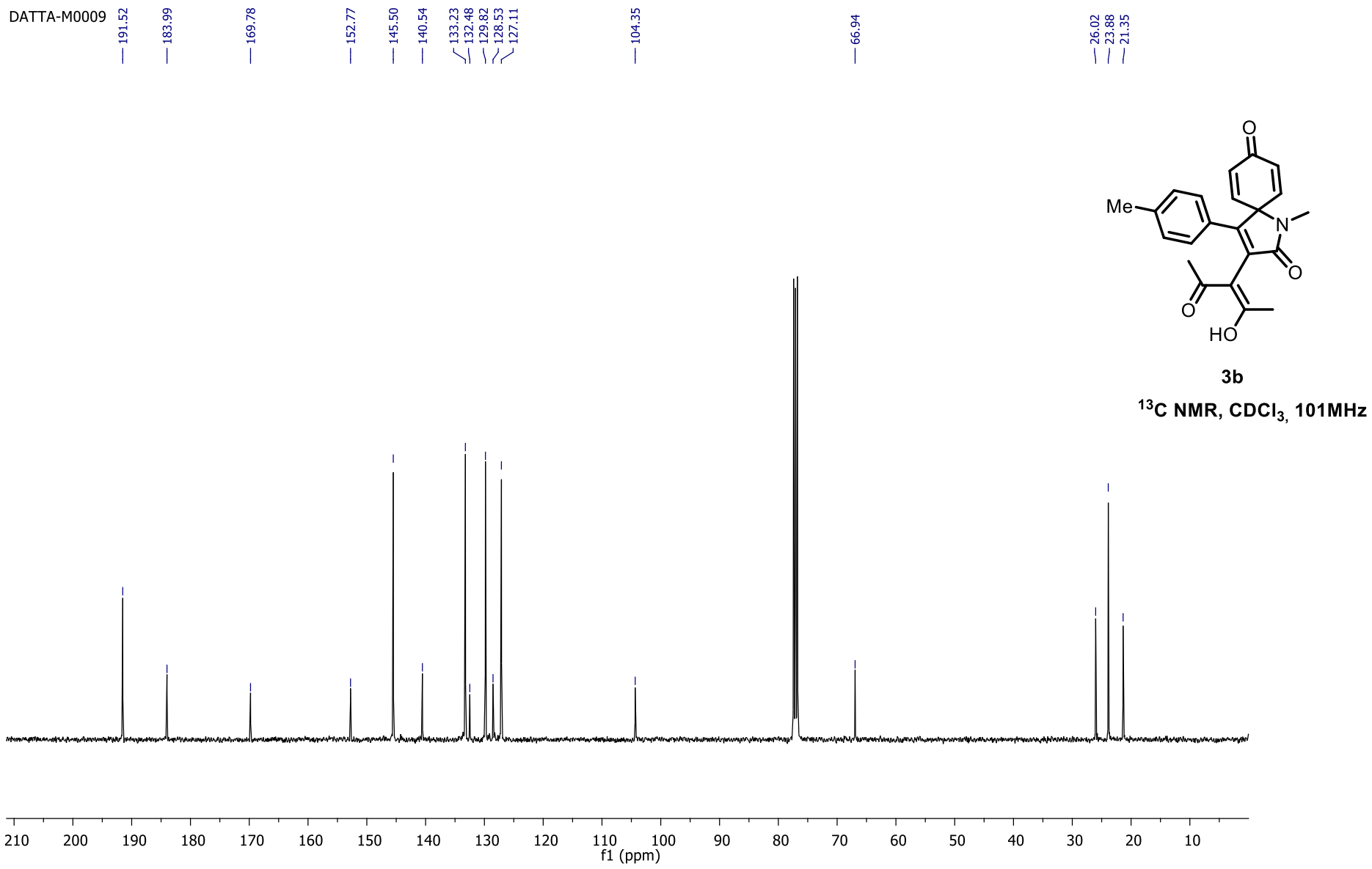

DATTA-M0009
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.27
7.27
7.26
7.26
7.25
7.25
6.56
6.55
6.55
6.53
2.94
1.96
O
N
O
O
HO
3a
1H NMR, CDCl3, 500MHz
3.45
2.89
4.26
3.00
5.80
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

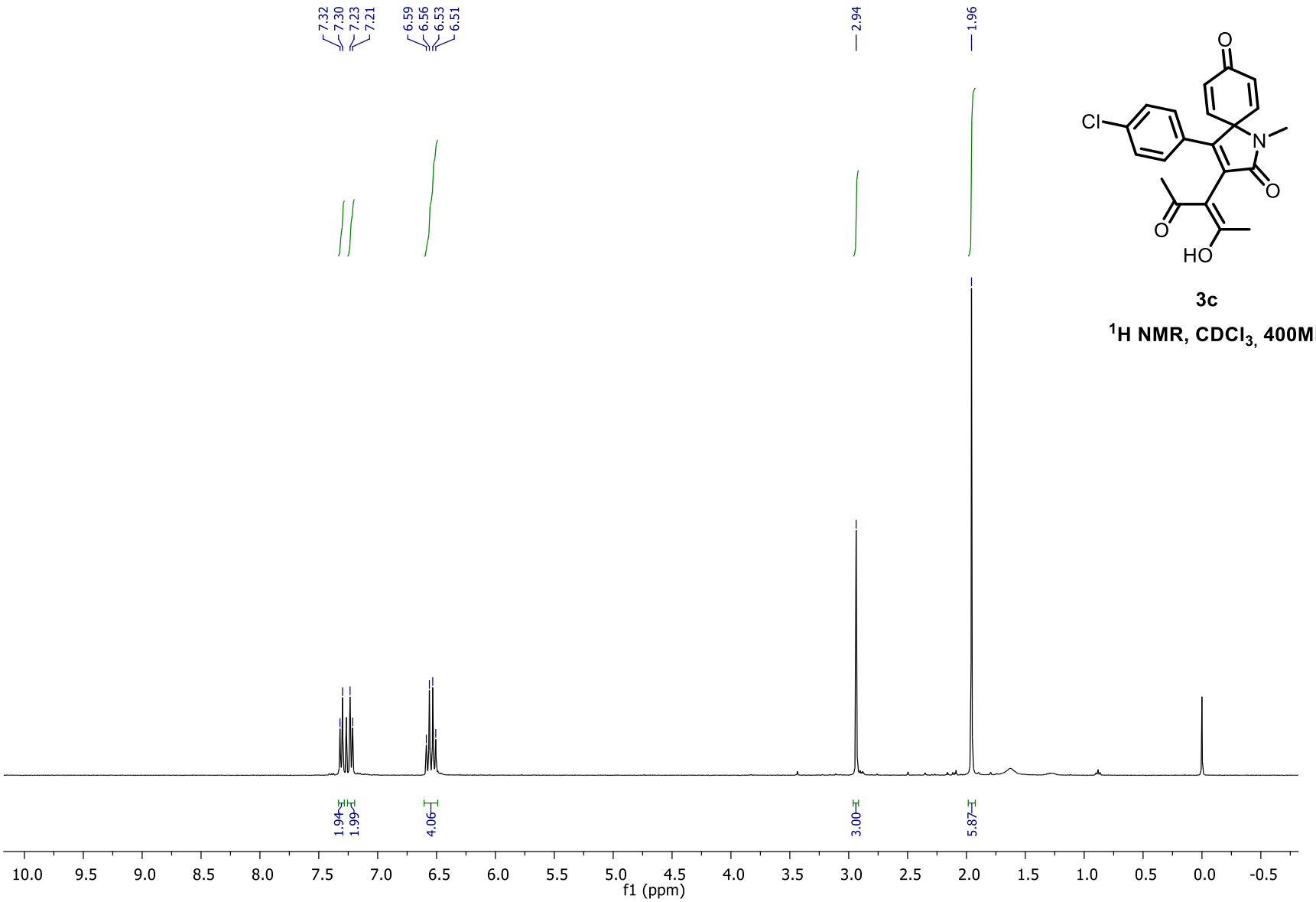

DATTA-M0009
191.48
183.86
169.62
152.75
145.24
133.35
133.25
131.47
130.14
129.11
127.24
104.17
67.01
26.08
23.88
O
N
O
O
HO
3a
13C NMR, CDCl3, 101MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3b

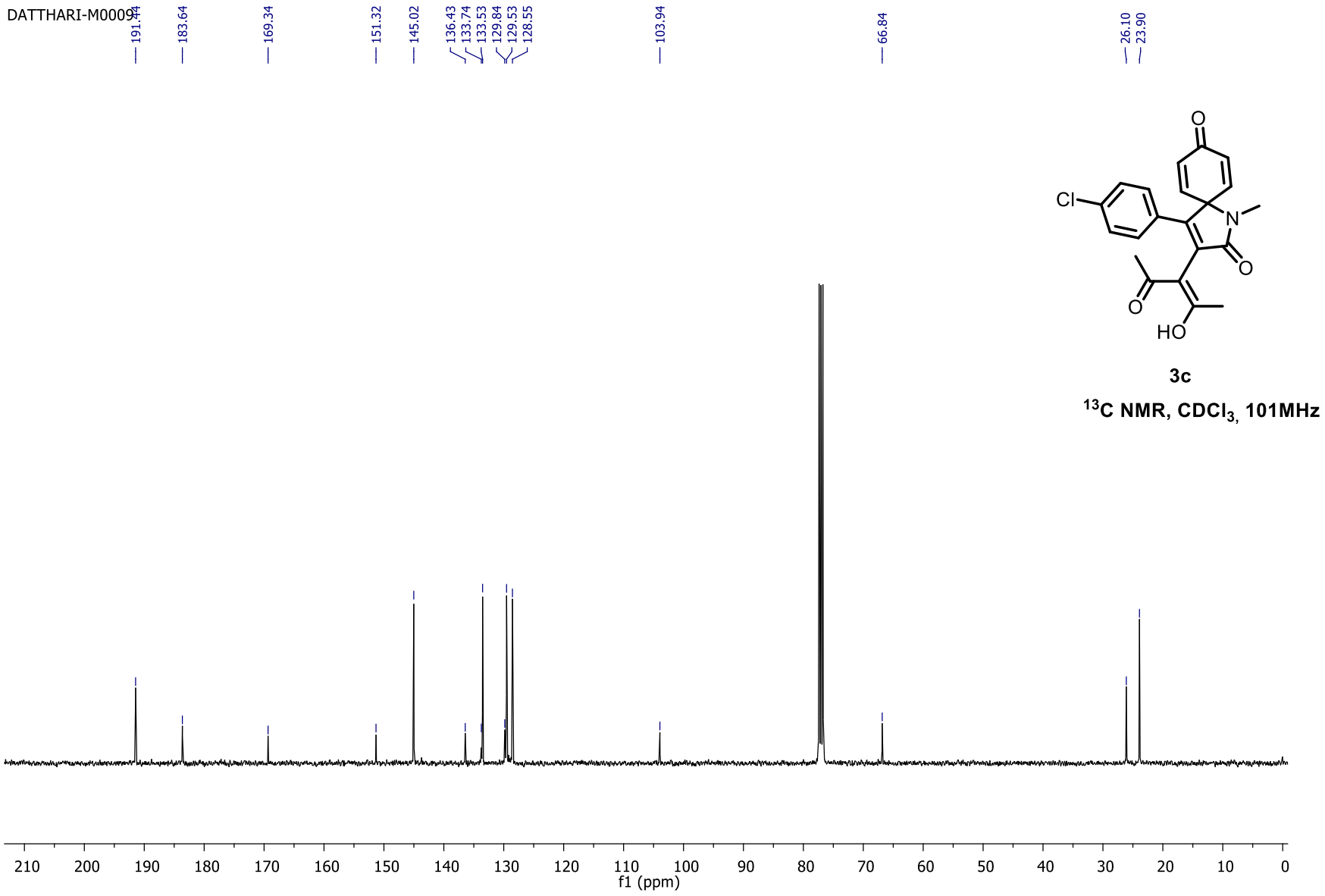
^{1}H NMR, $CDCl_3$, 500MHz


DATTA-M0009
191.52
183.99
169.78
152.77
145.50
140.54
133.23
132.48
129.82
128.53
127.11
104.35
66.94
26.02
23.88
21.35
Me
N
O
O
O
HO
3b
13C NMR, CDCl3, 101MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



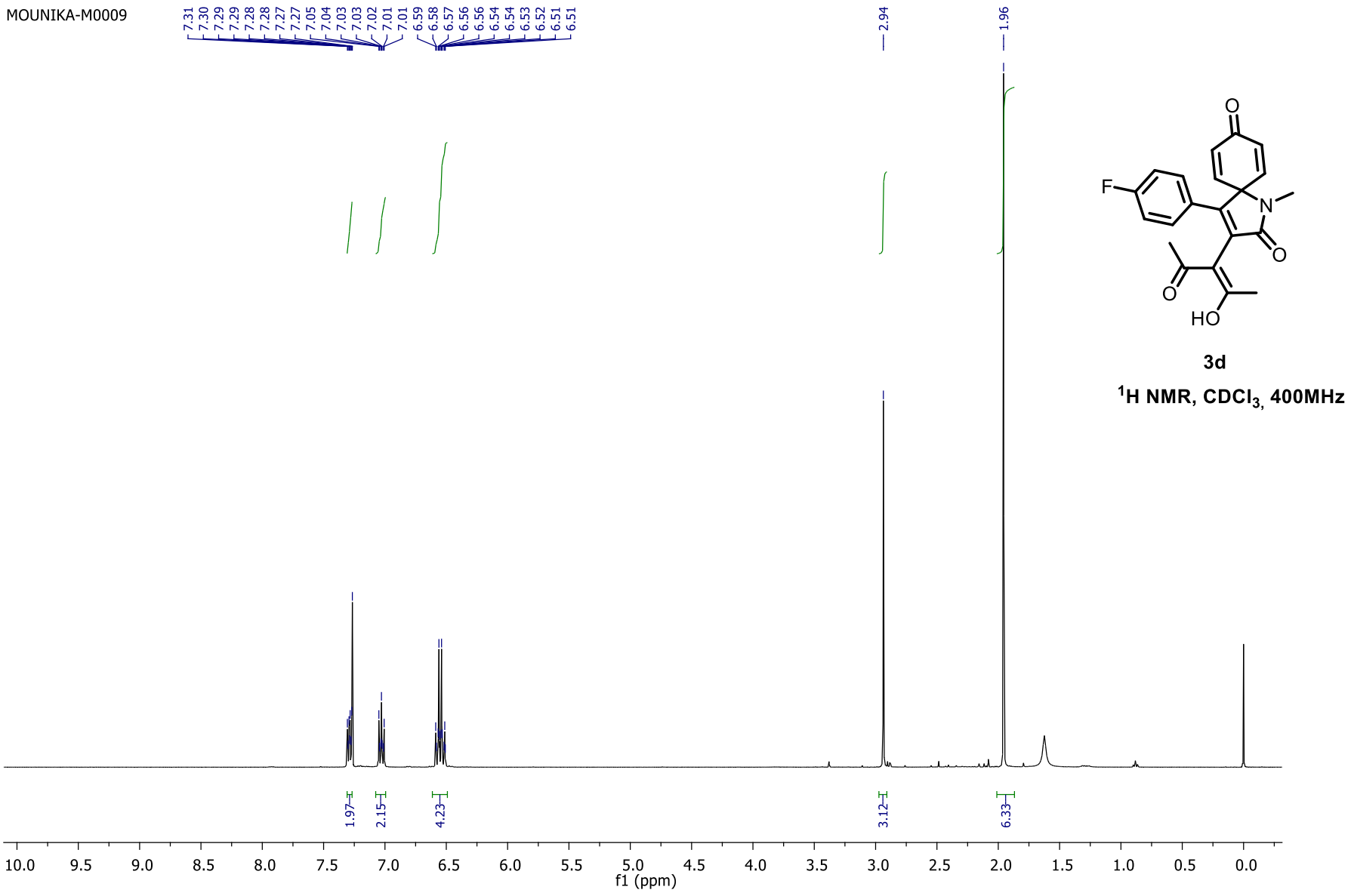
3c

^{1}H NMR, $CDCl_3$, 400MHz



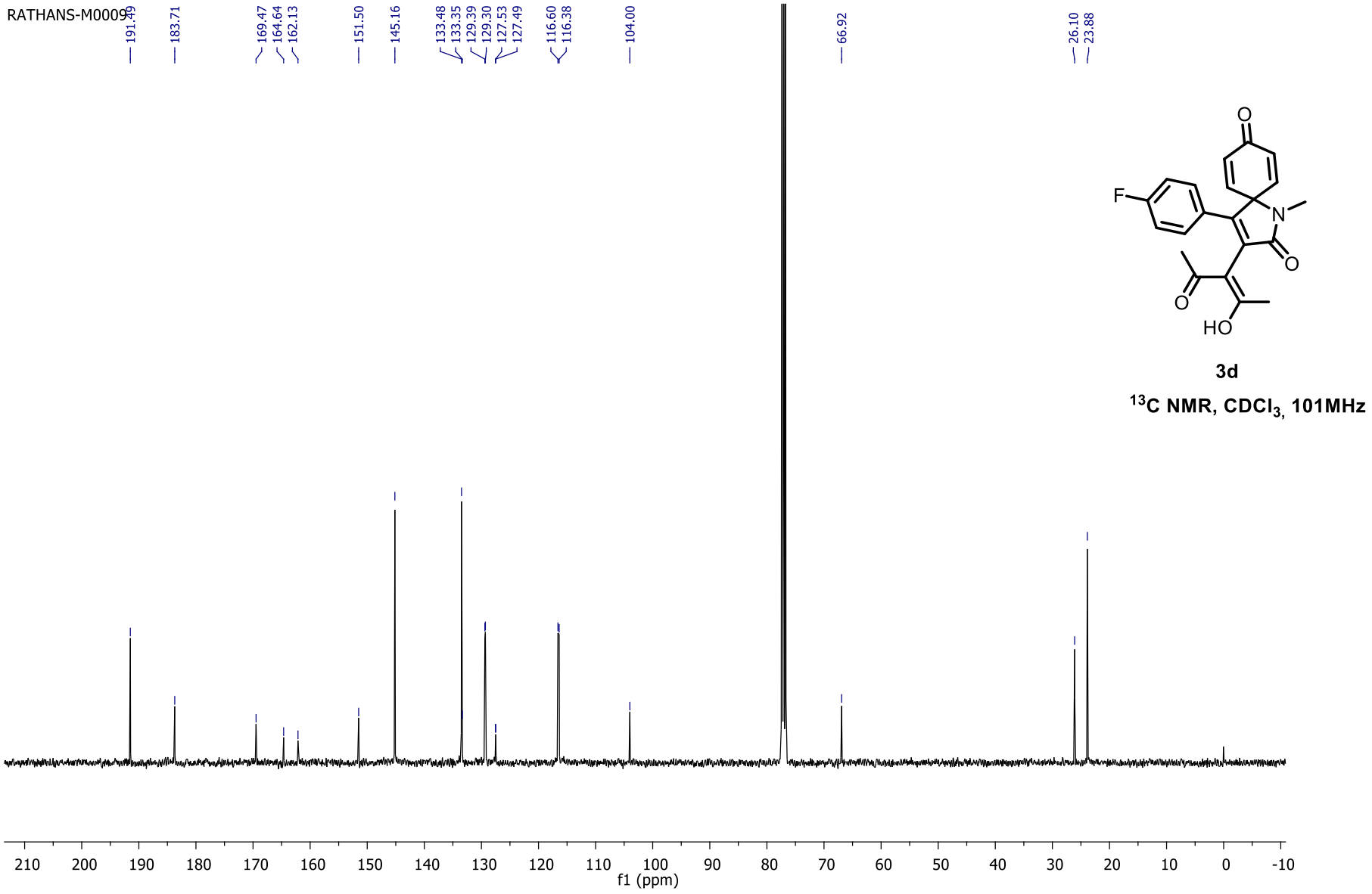
3c

^{13}C NMR, $CDCl_3$, 101MHz



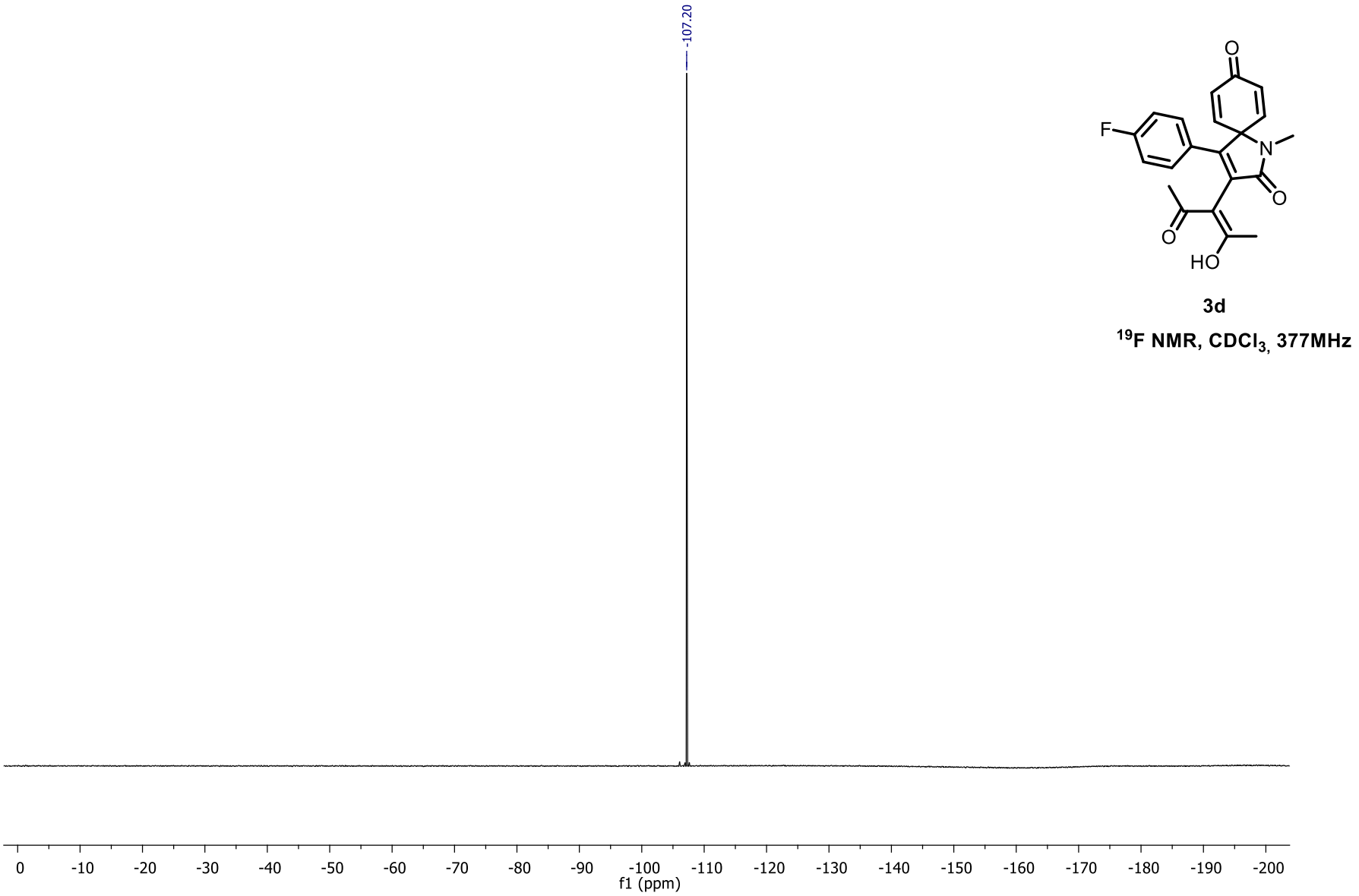
3d

^{1}H NMR, $CDCl_3$, 400MHz



3d

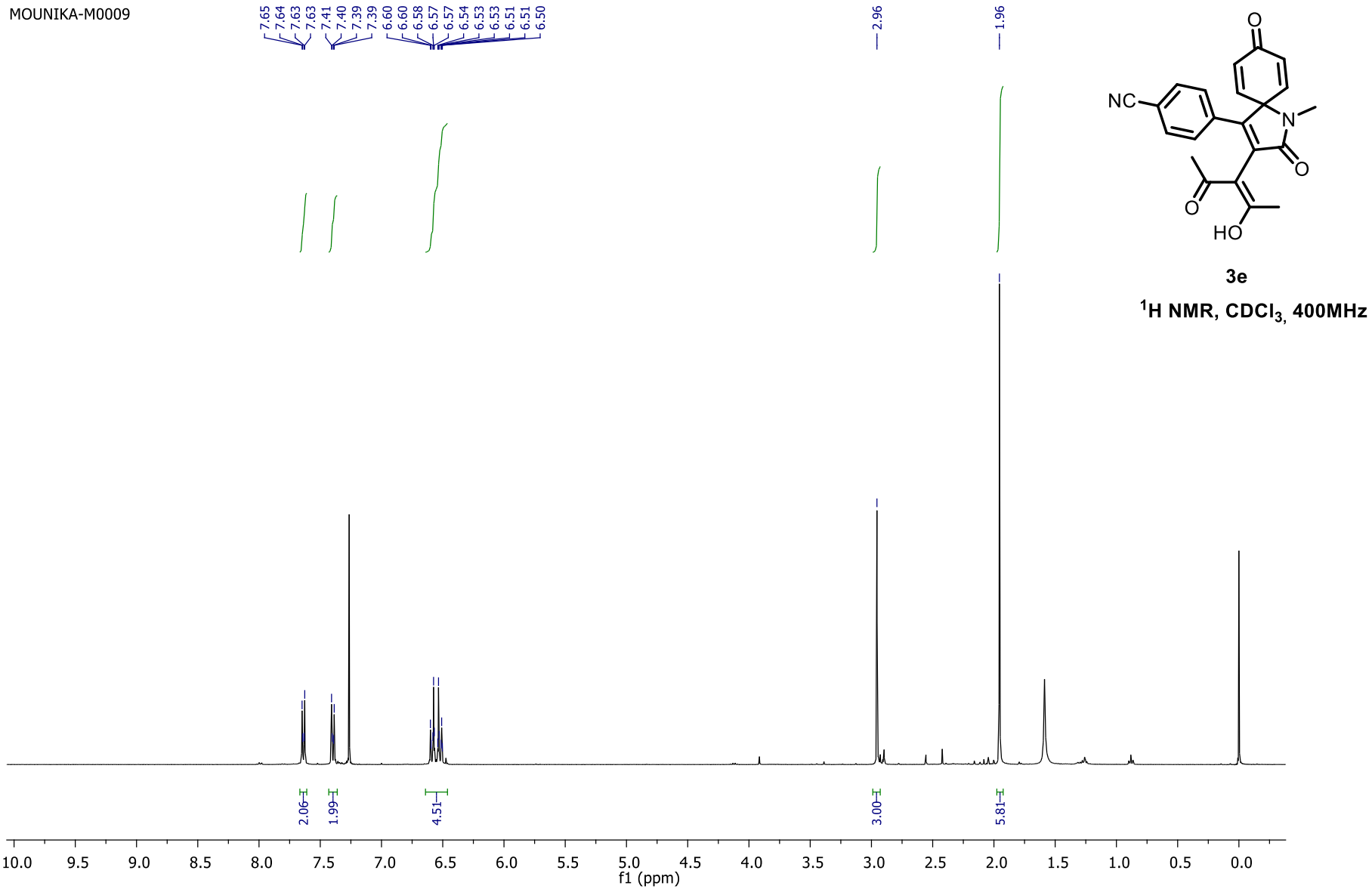
^{13}C NMR, $CDCl_3$, 101MHz



3d

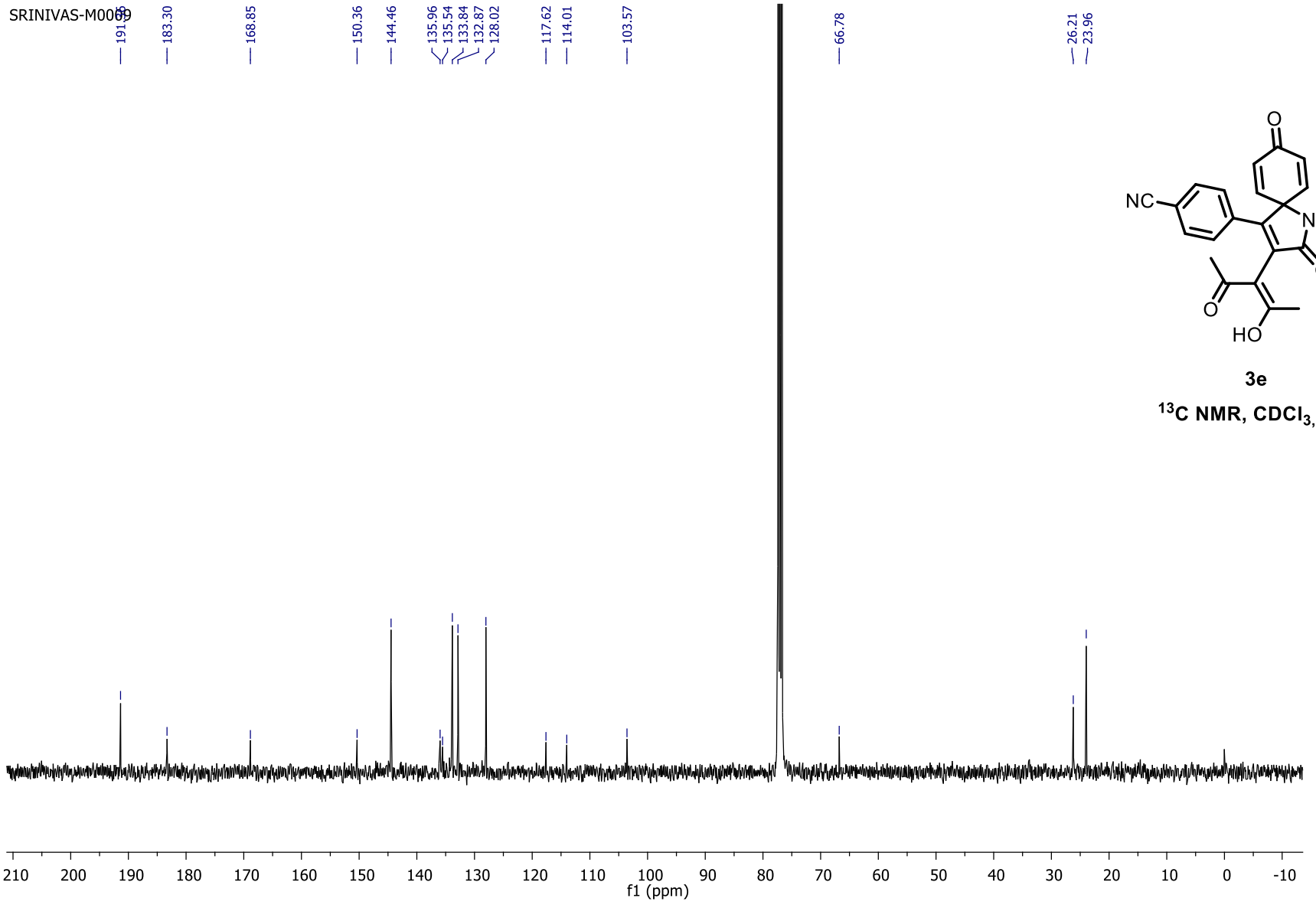
^{19}F NMR, $CDCl_3$, 377MHz

MOUNIKA-M0009



3e

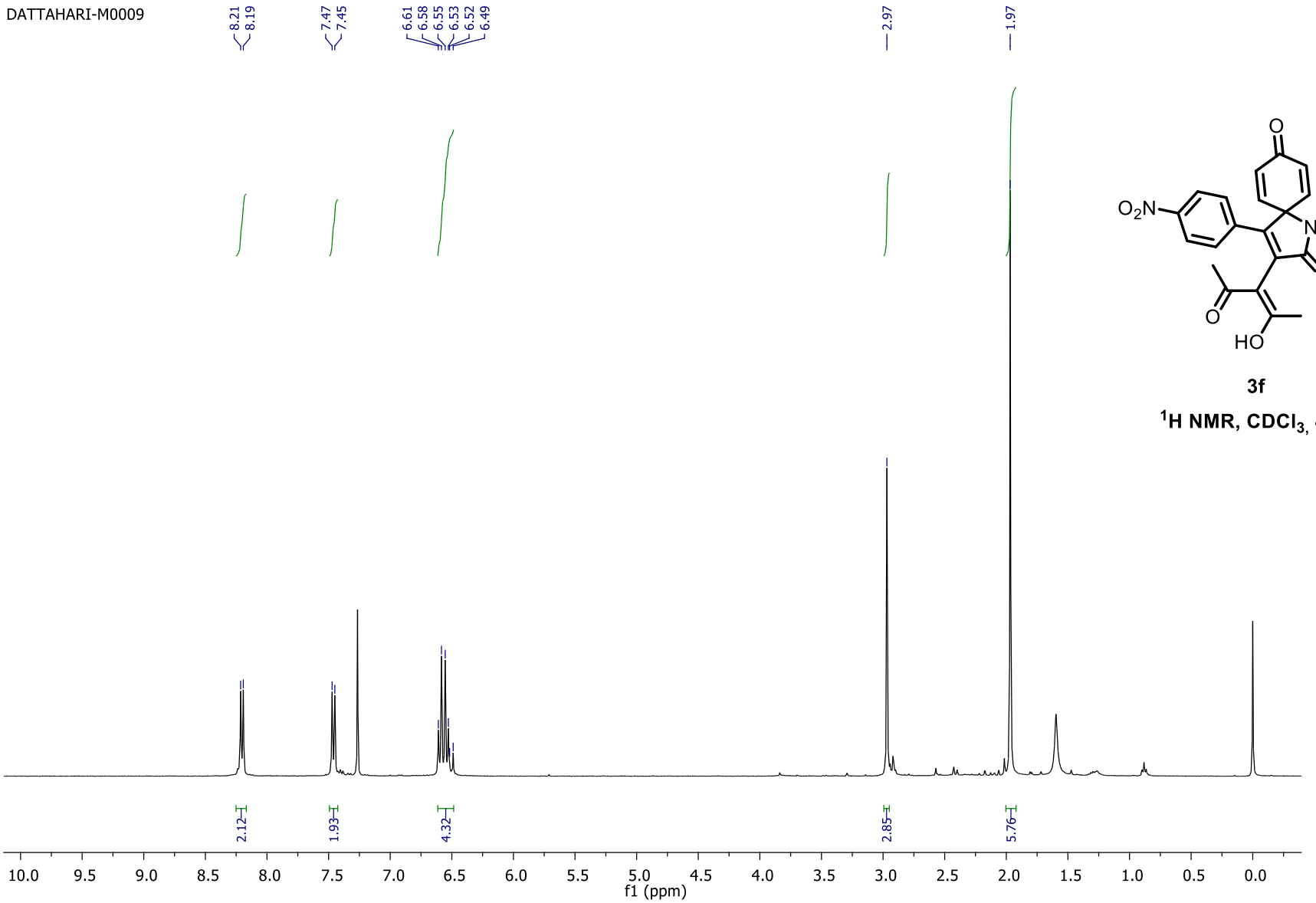
^{1}H NMR, $CDCl_3$, 400MHz



3e

^{13}C NMR, $CDCl_3$, 101MHz

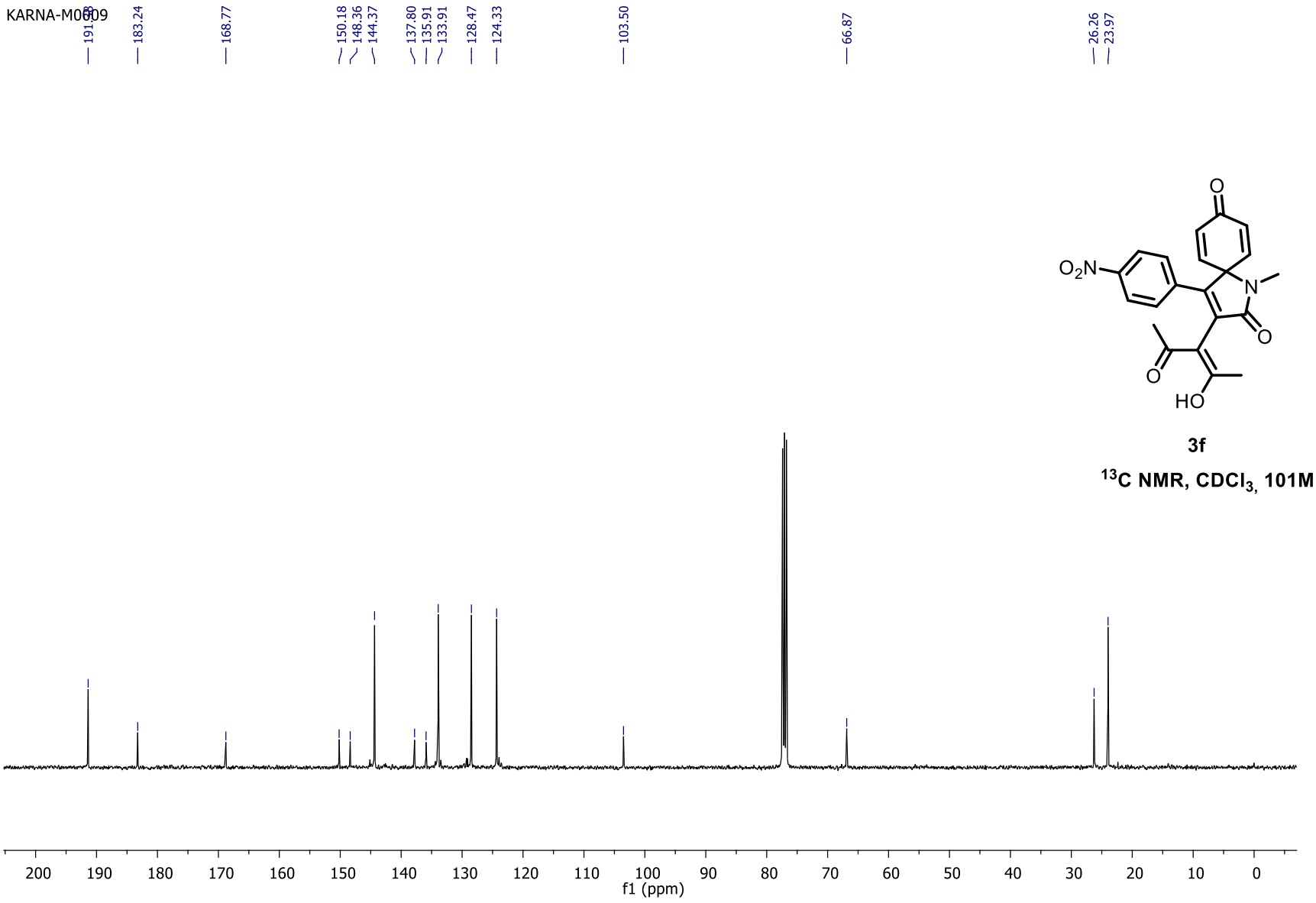
DATTAHARI-M0009



3f

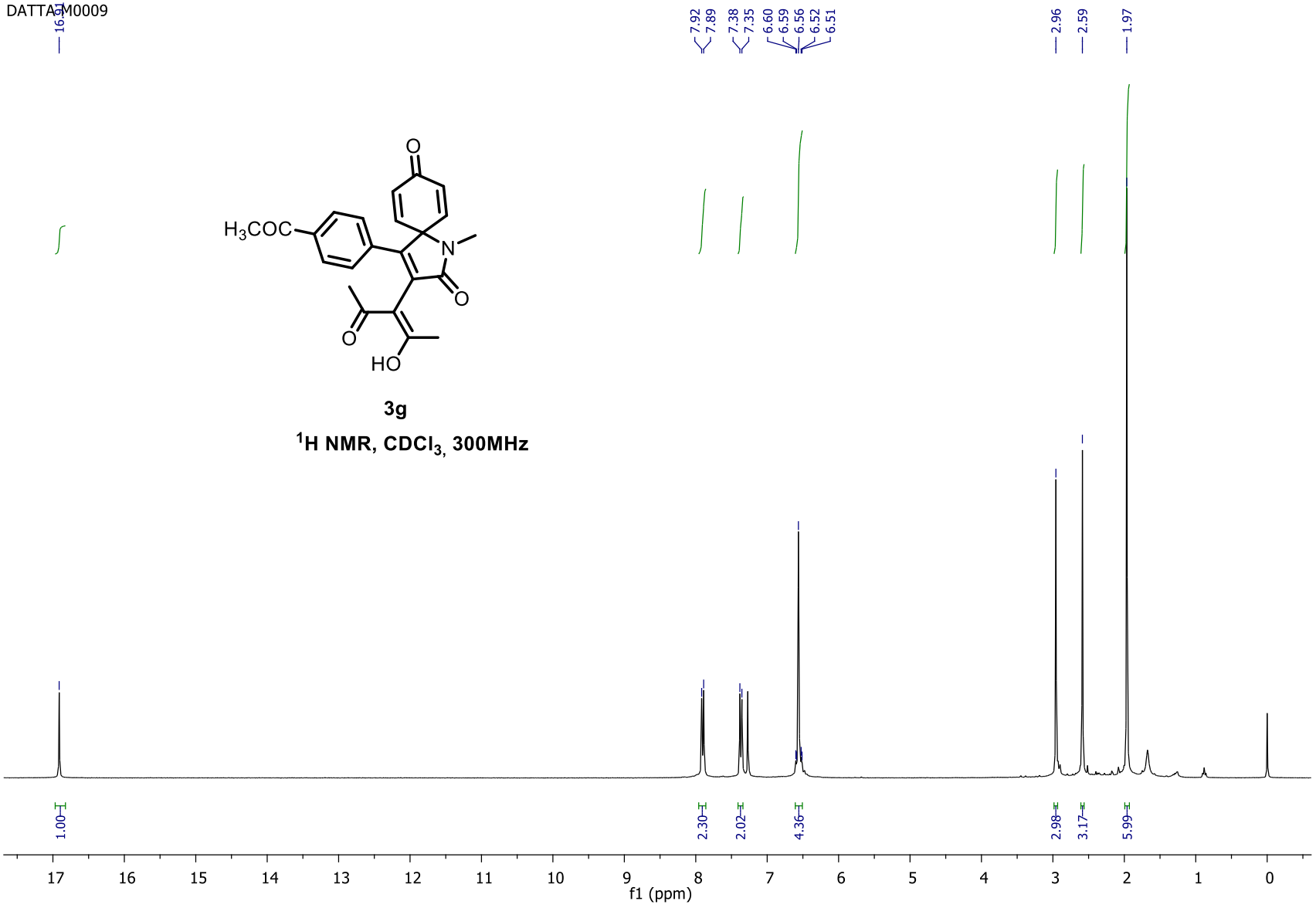
^{1}H NMR, $CDCl_3$, 400MHz

KARNA-M0609



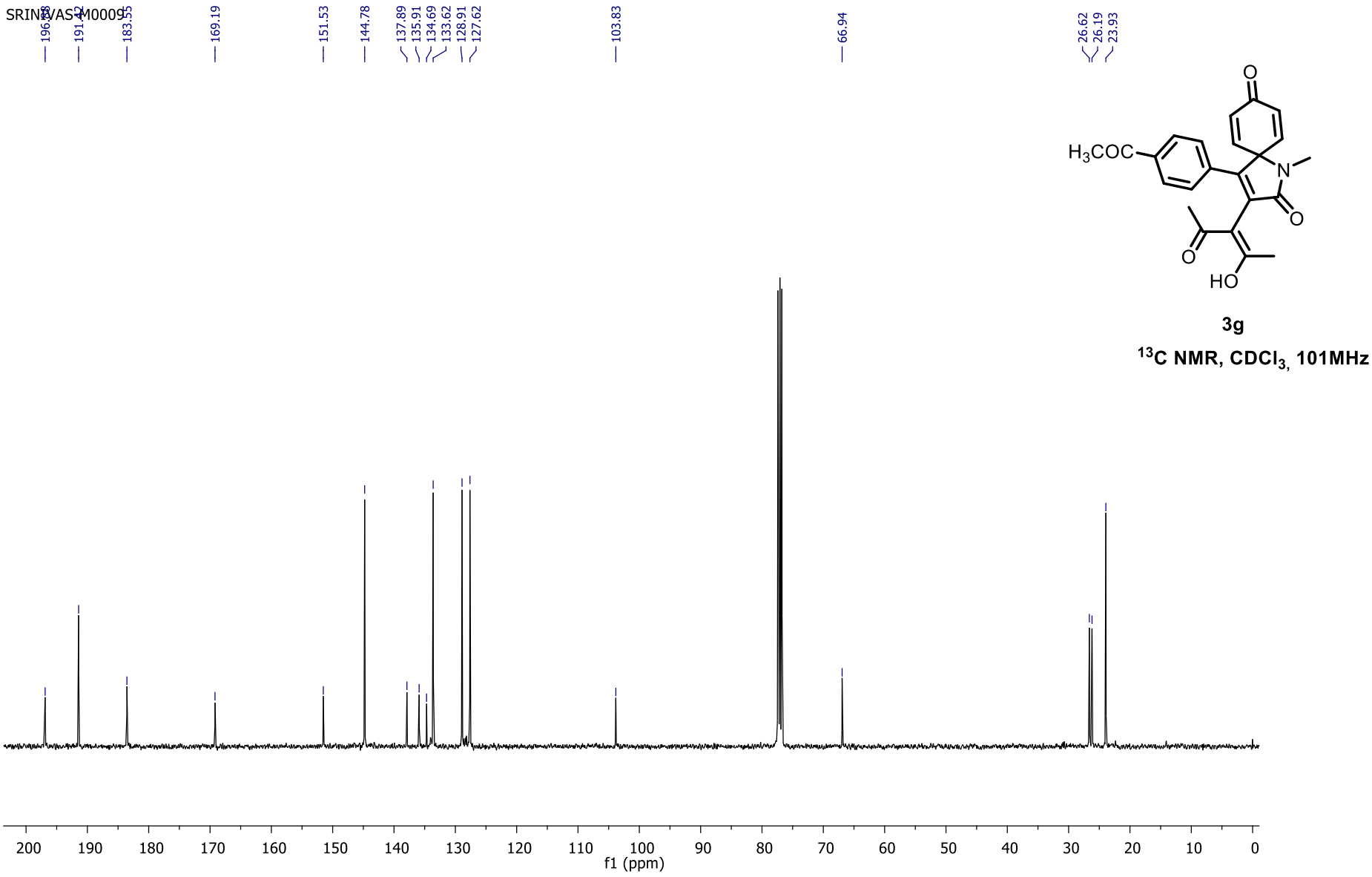
3f

^{13}C NMR, $CDCl_3$, 101MHz



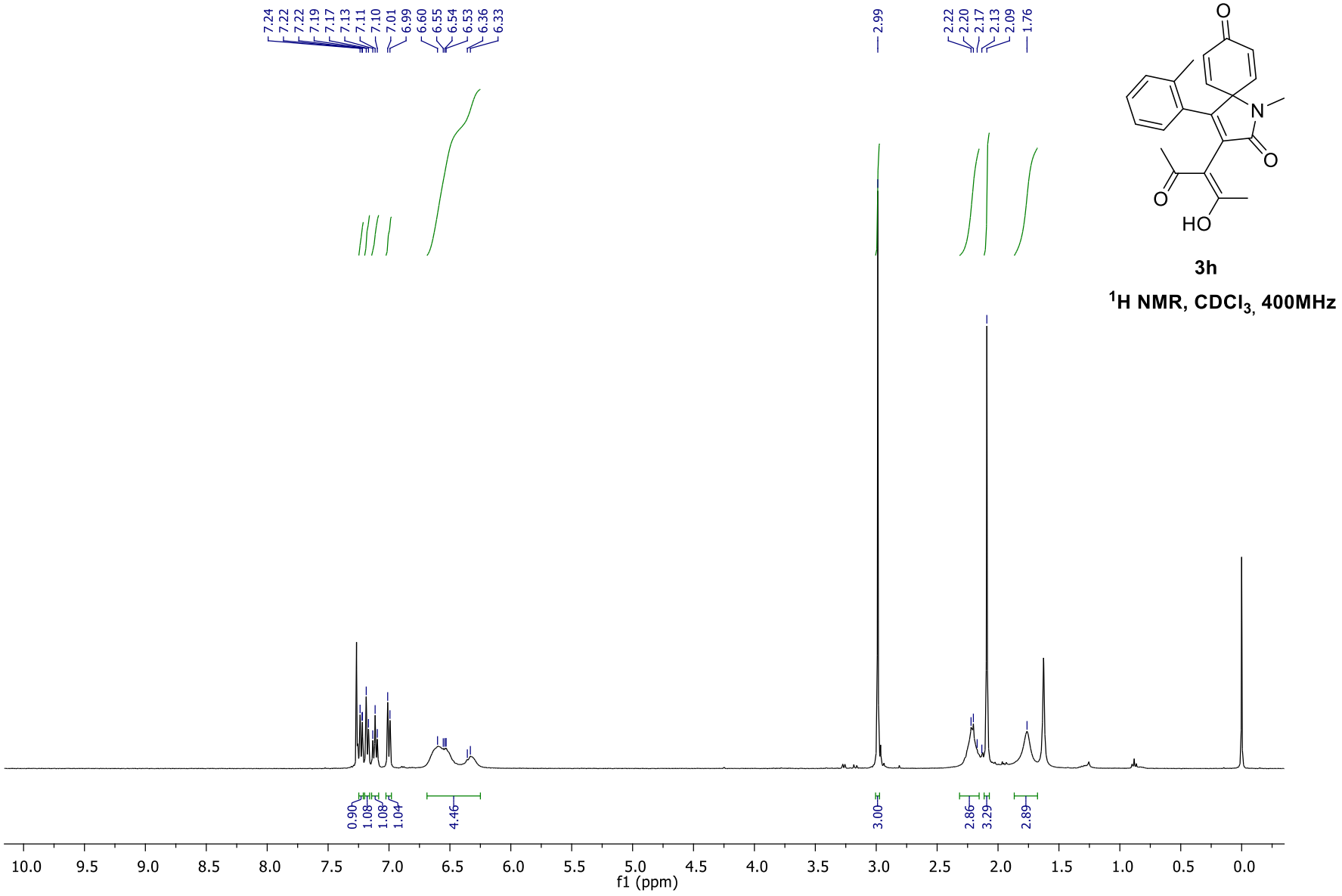
3g

^{1}H NMR, $CDCl_3$, 300MHz



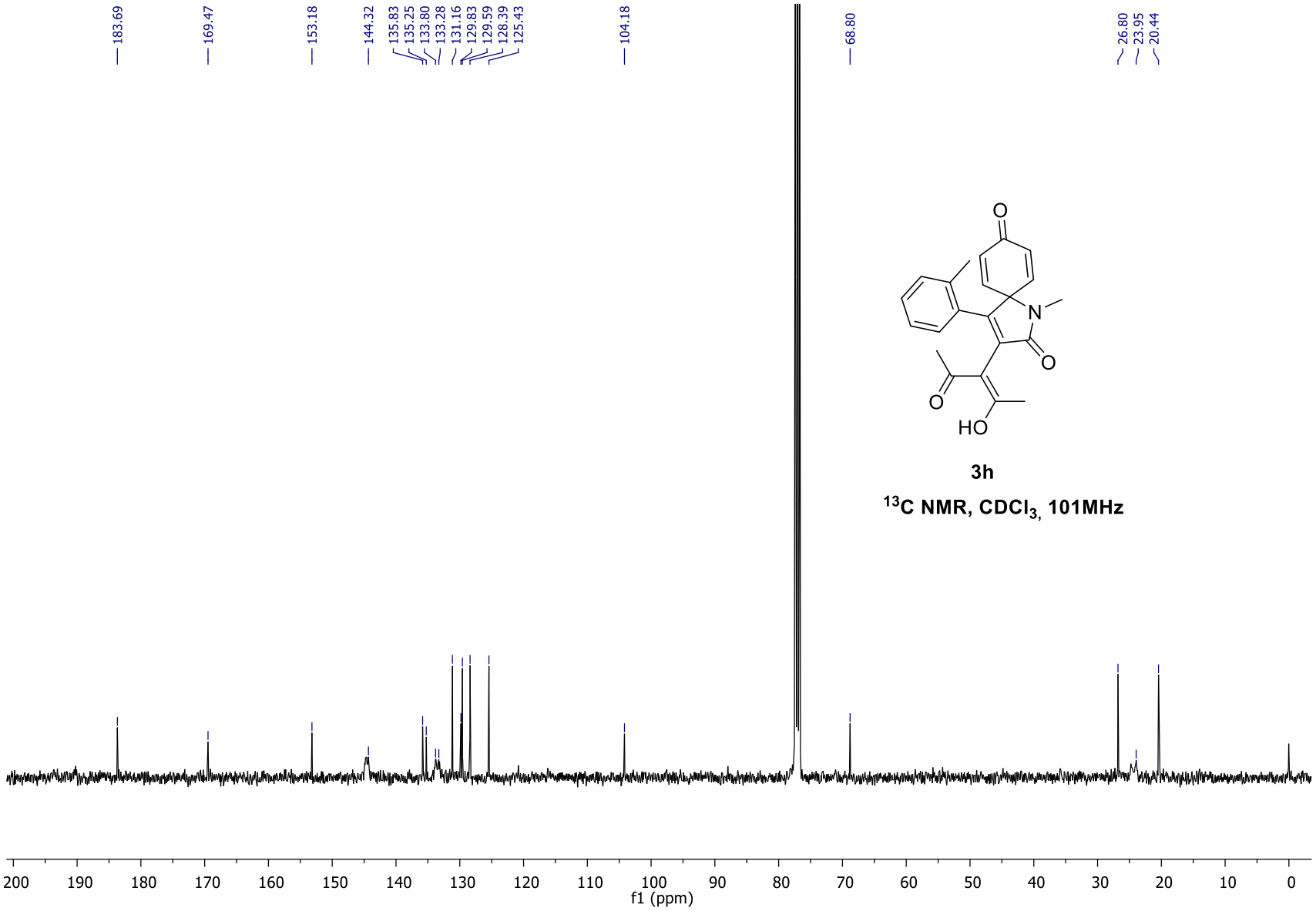
3g

^{13}C NMR, $CDCl_3$, 101MHz



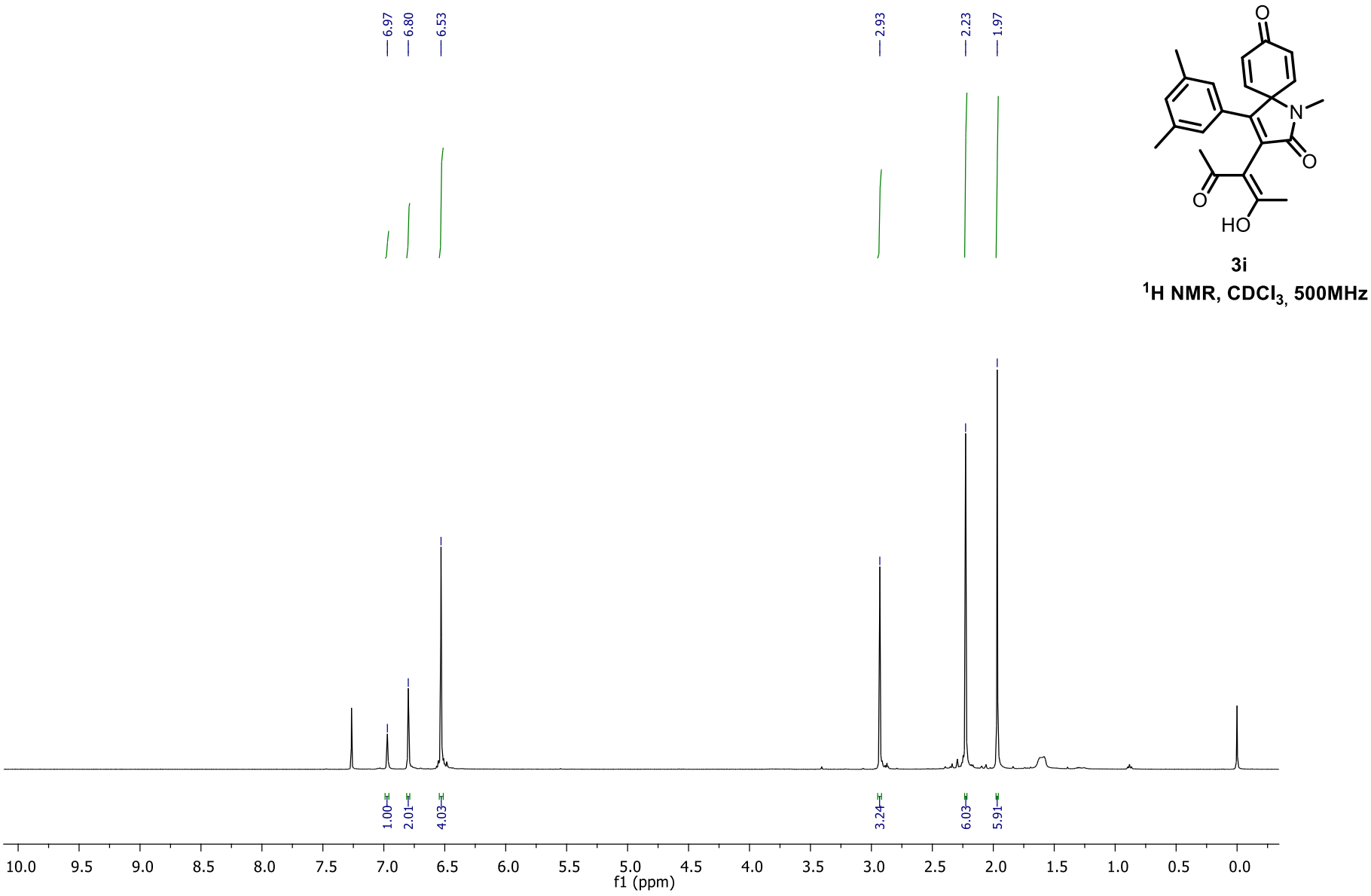
3h

^{1}H NMR, $CDCl_3$, 400MHz



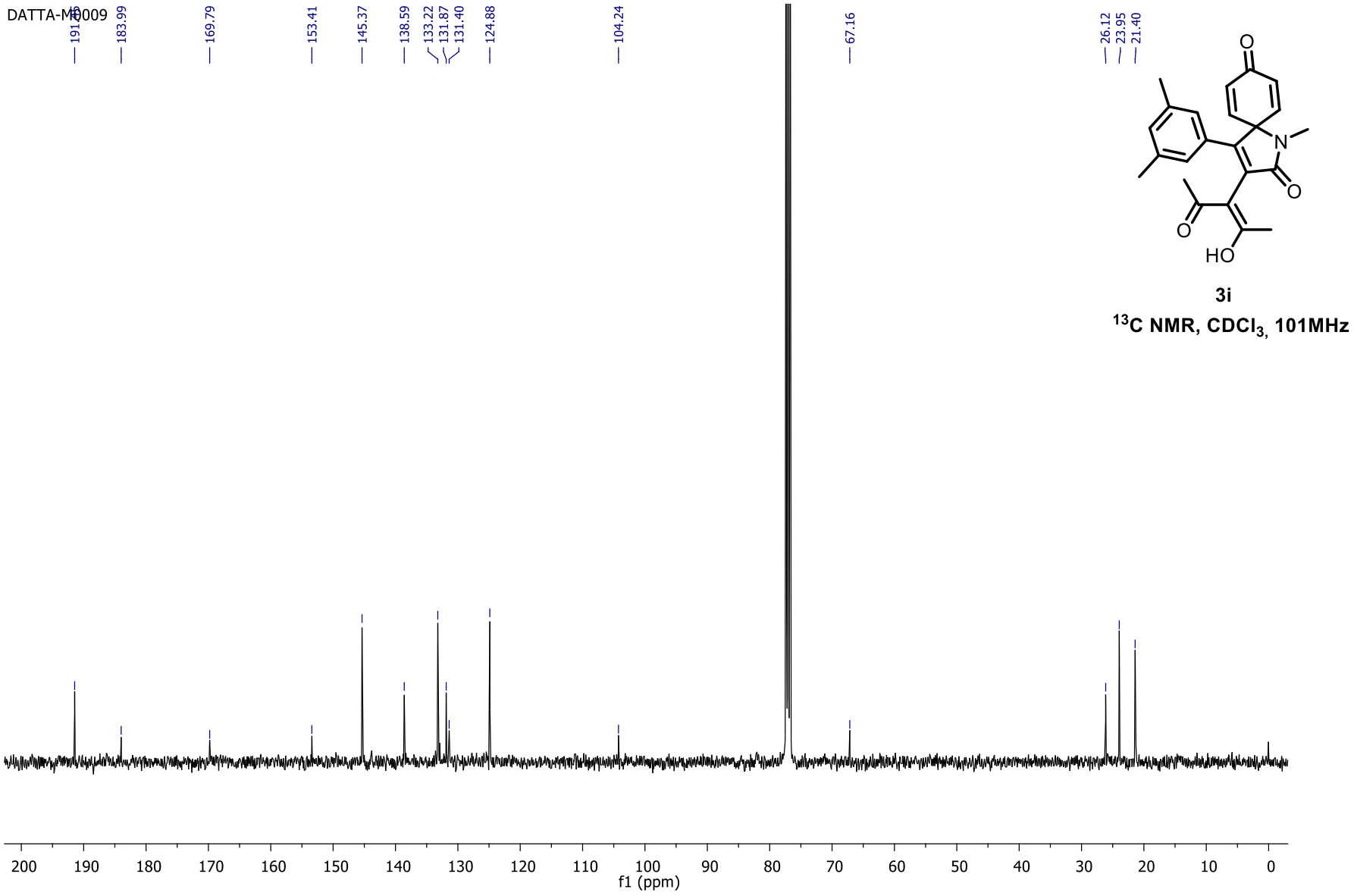
3h

^{13}C NMR, $CDCl_3$, 101MHz



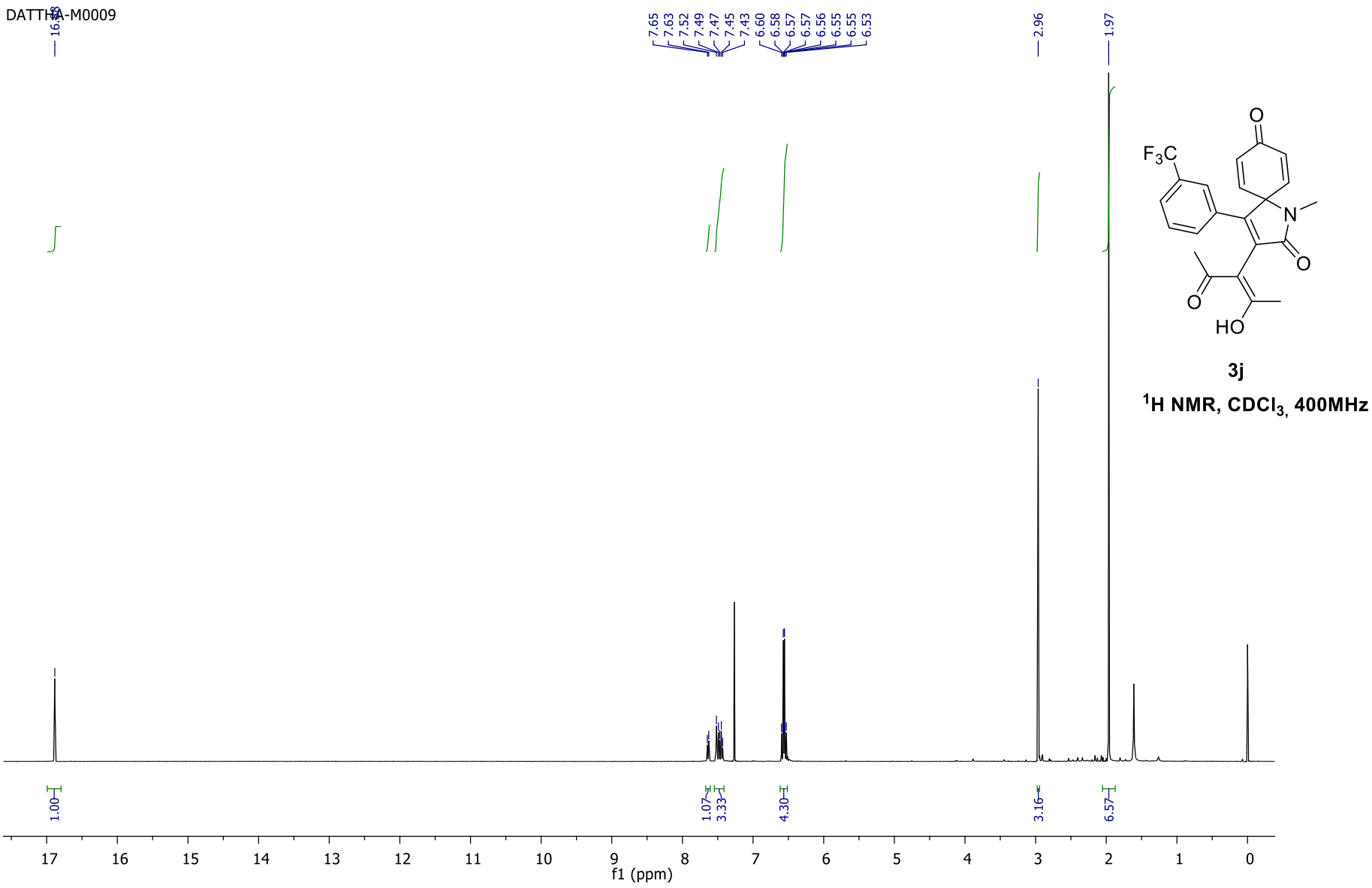
3i

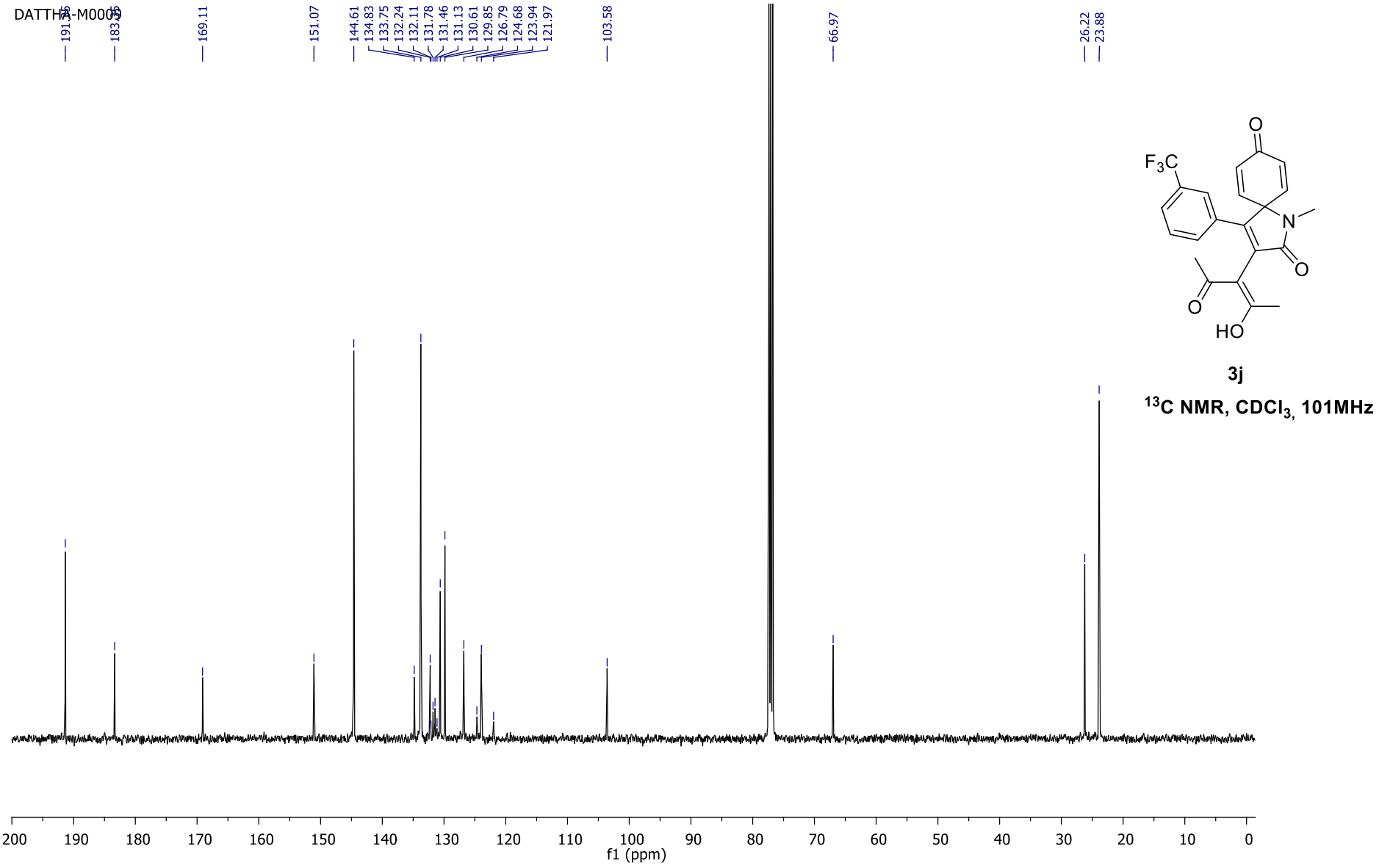
^{1}H NMR, $CDCl_3$, 500MHz

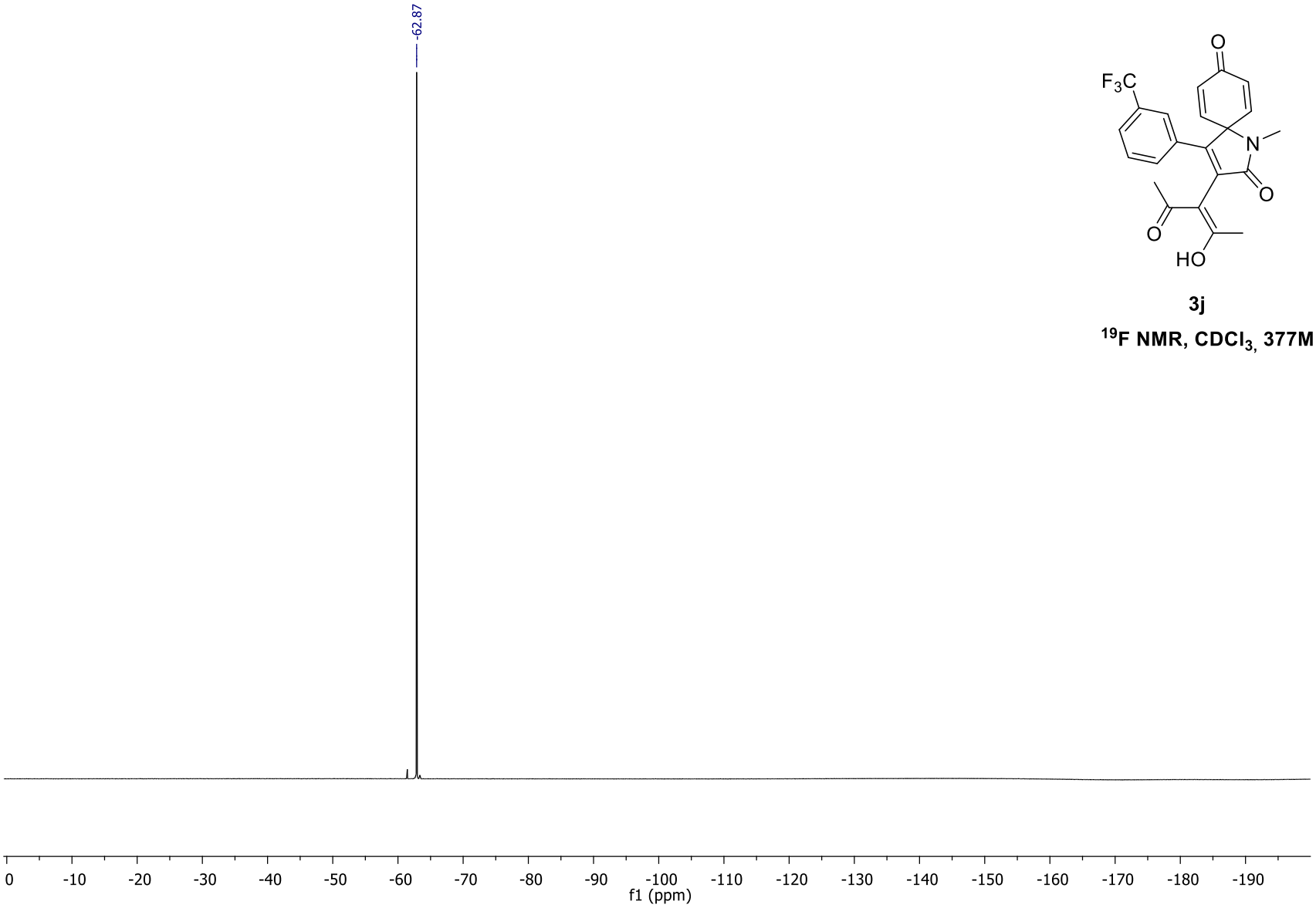


3i

^{13}C NMR, $CDCl_3$, 101MHz

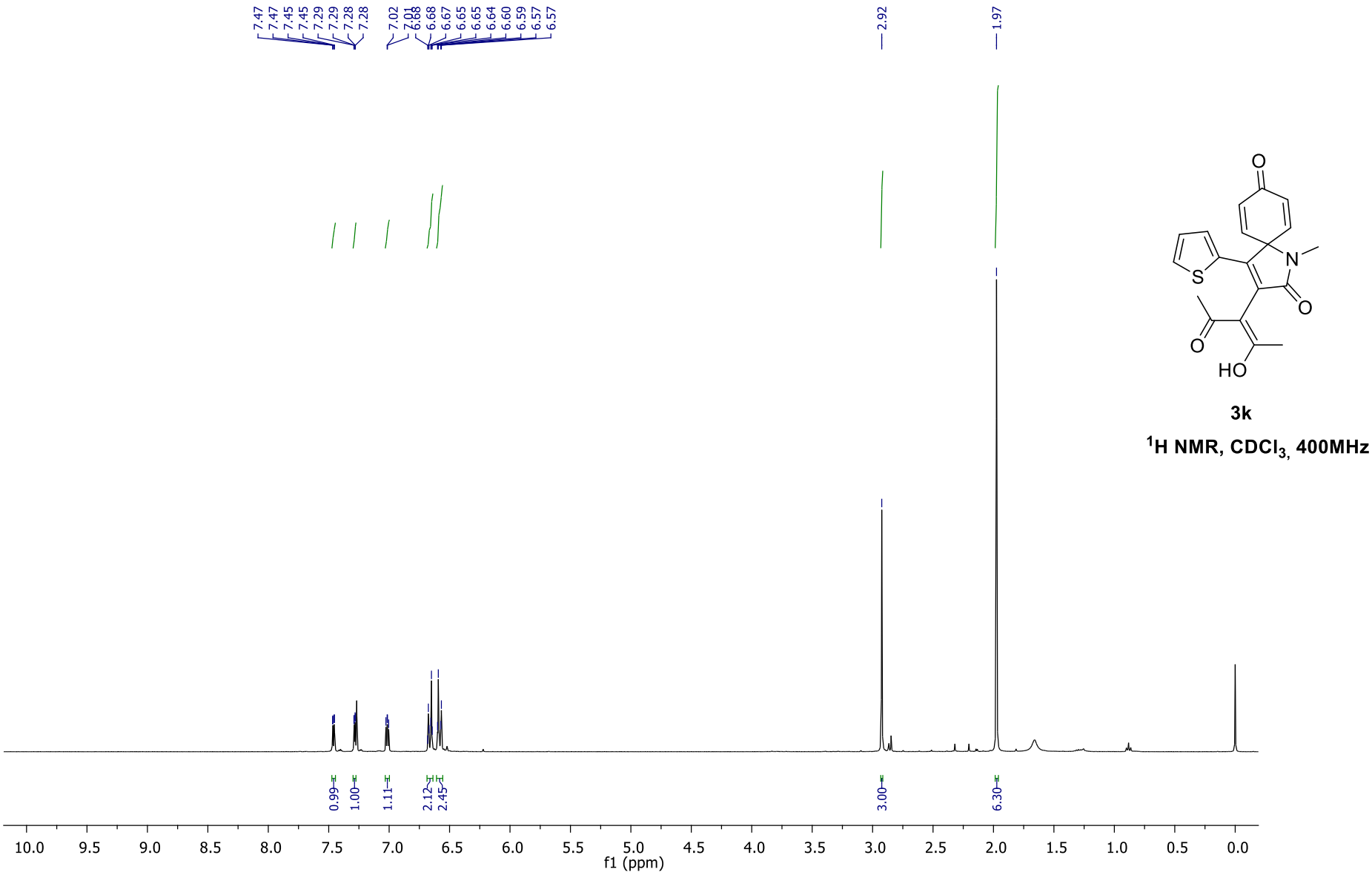

DATTHA-M0009
16.93
7.65
7.63
7.52
7.49
7.47
7.45
7.43
6.60
6.58
6.57
6.57
6.56
6.55
6.55
6.53
2.96
1.97
1.00
1.07
3.33
4.30
3.16
6.57
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
F3C
O
N
O
O
HO
3j
1H NMR, CDCl3, 400MHz


DATTHA-M0009
191.15
183.59
169.11
151.07
144.61
134.83
133.75
132.24
132.11
131.78
131.46
131.13
130.61
129.85
126.79
124.68
123.94
121.97
103.58
66.97
26.22
23.88
F3C
O
N
O
O
HO
3j
13C NMR, CDCl3, 101MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



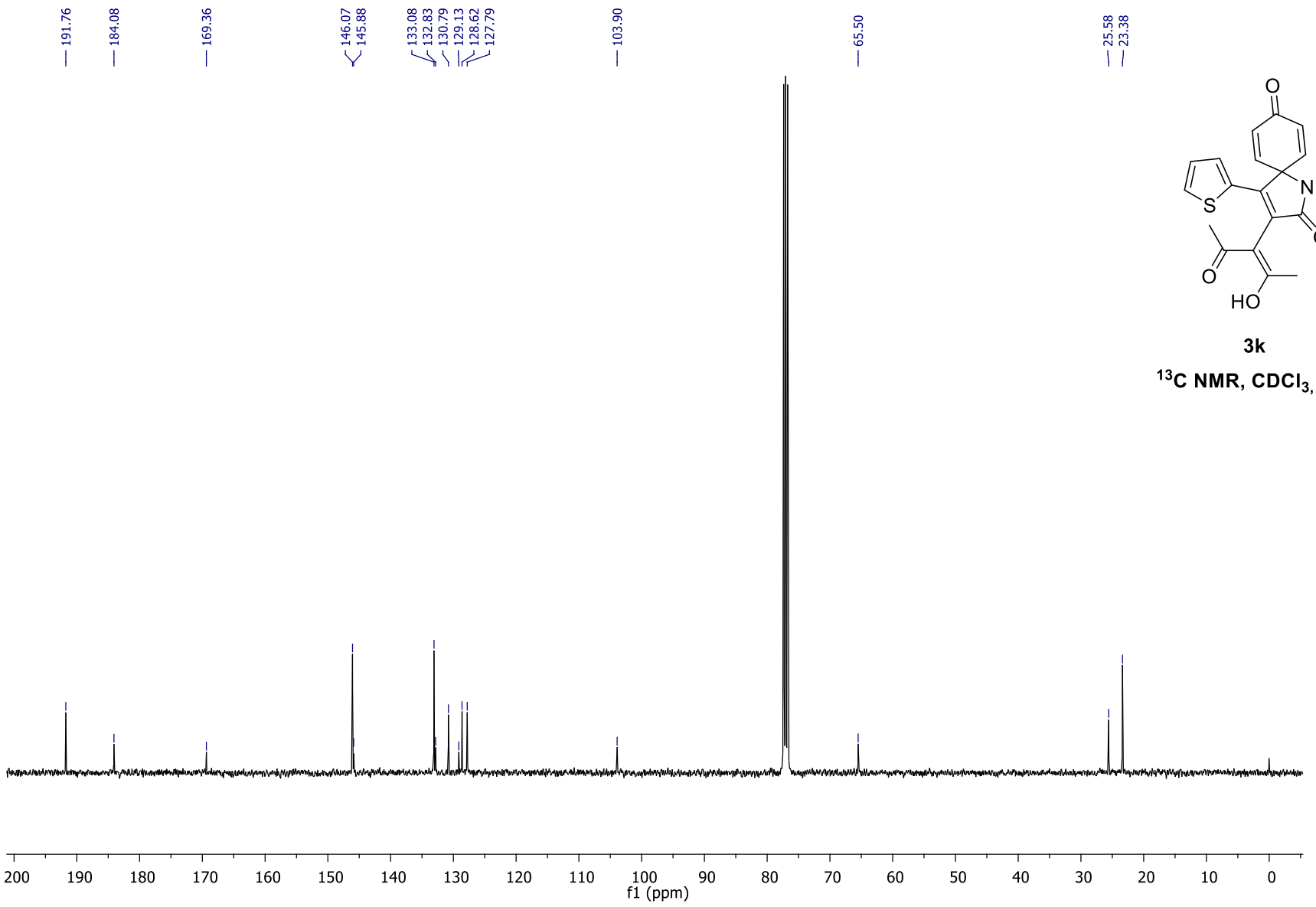
3j

^{19}F NMR, $CDCl_3$, 377MHz



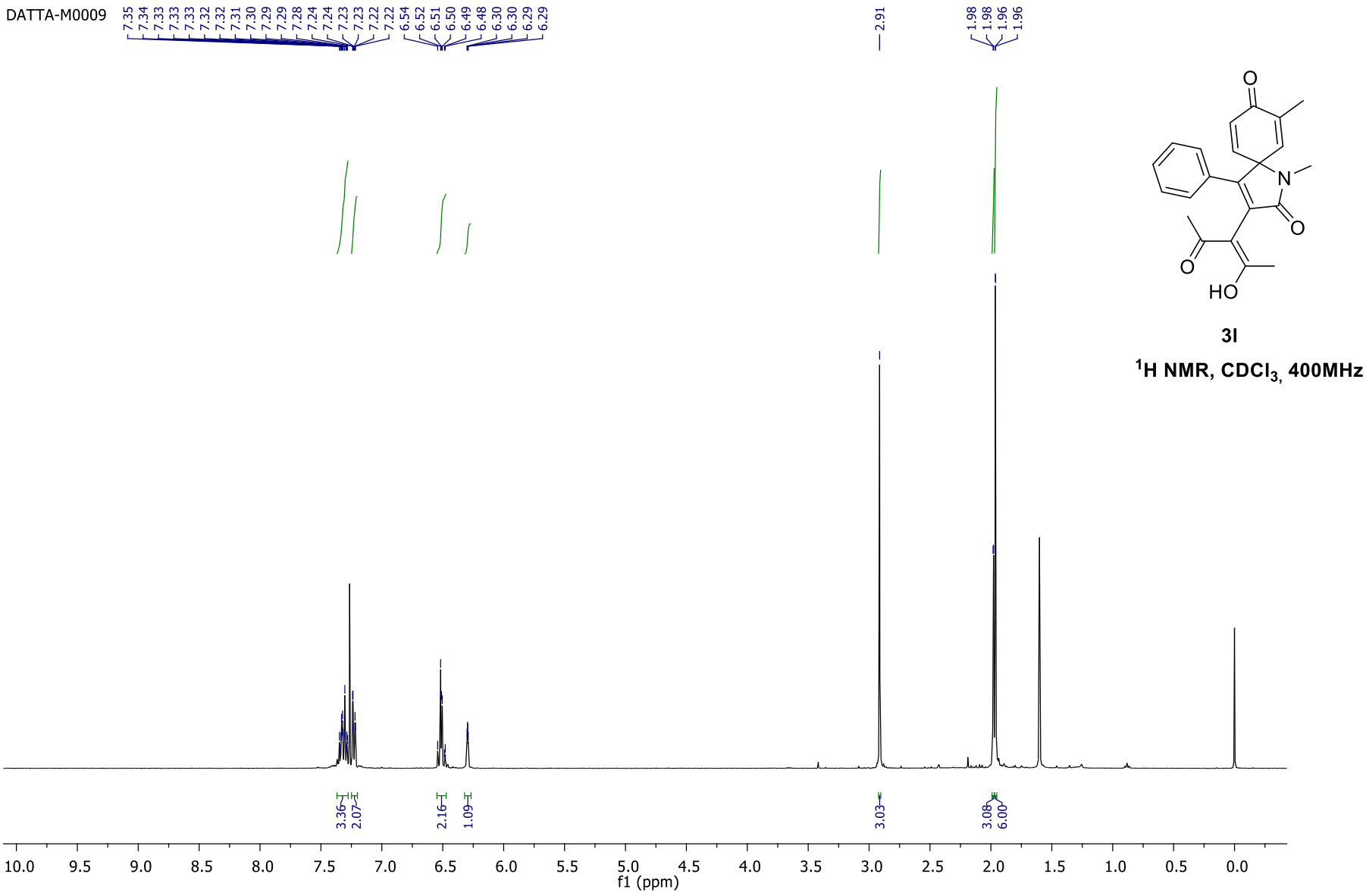
3k

^{1}H NMR, $CDCl_3$, 400MHz



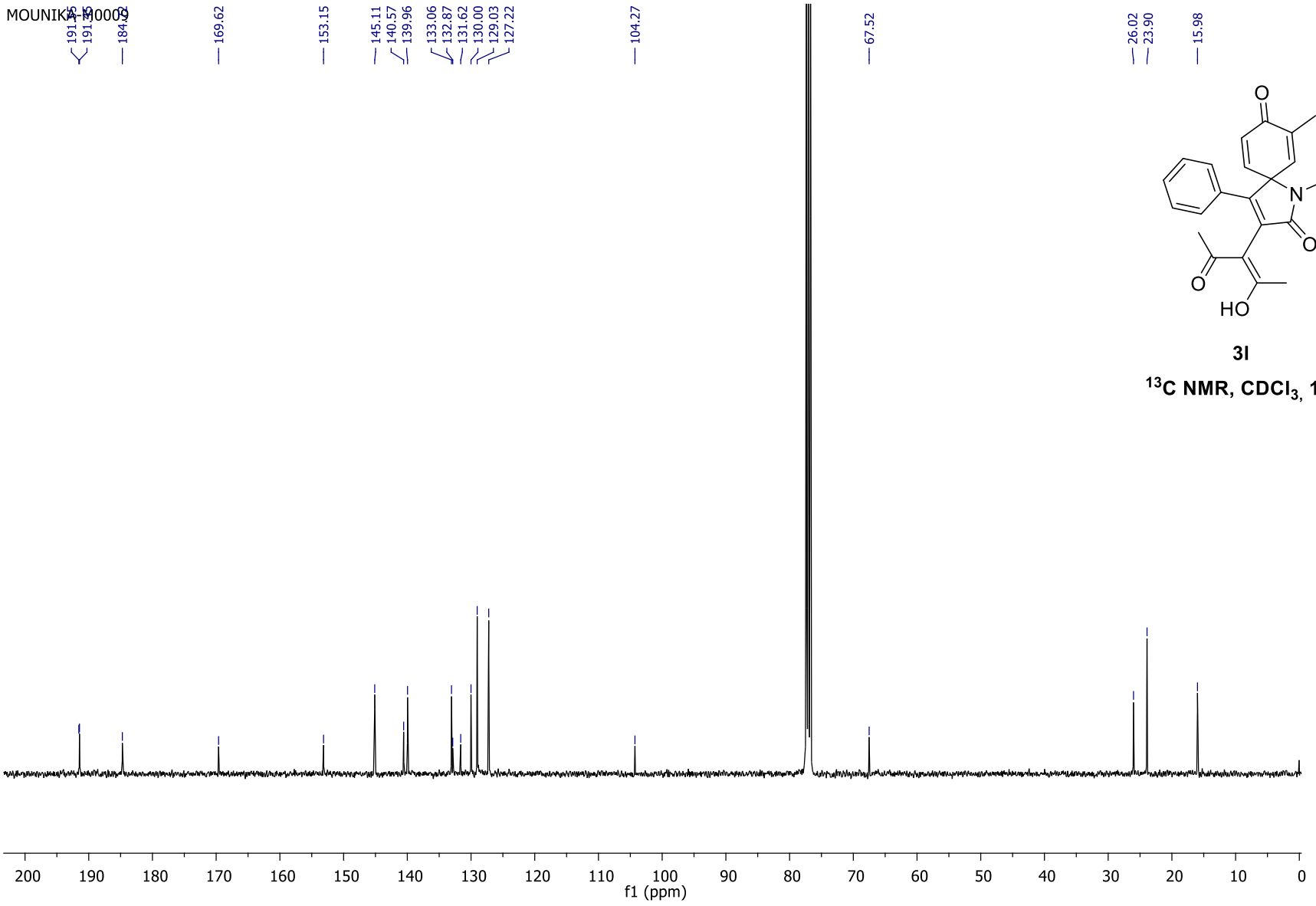
3k

^{13}C NMR, $CDCl_3$, 101MHz



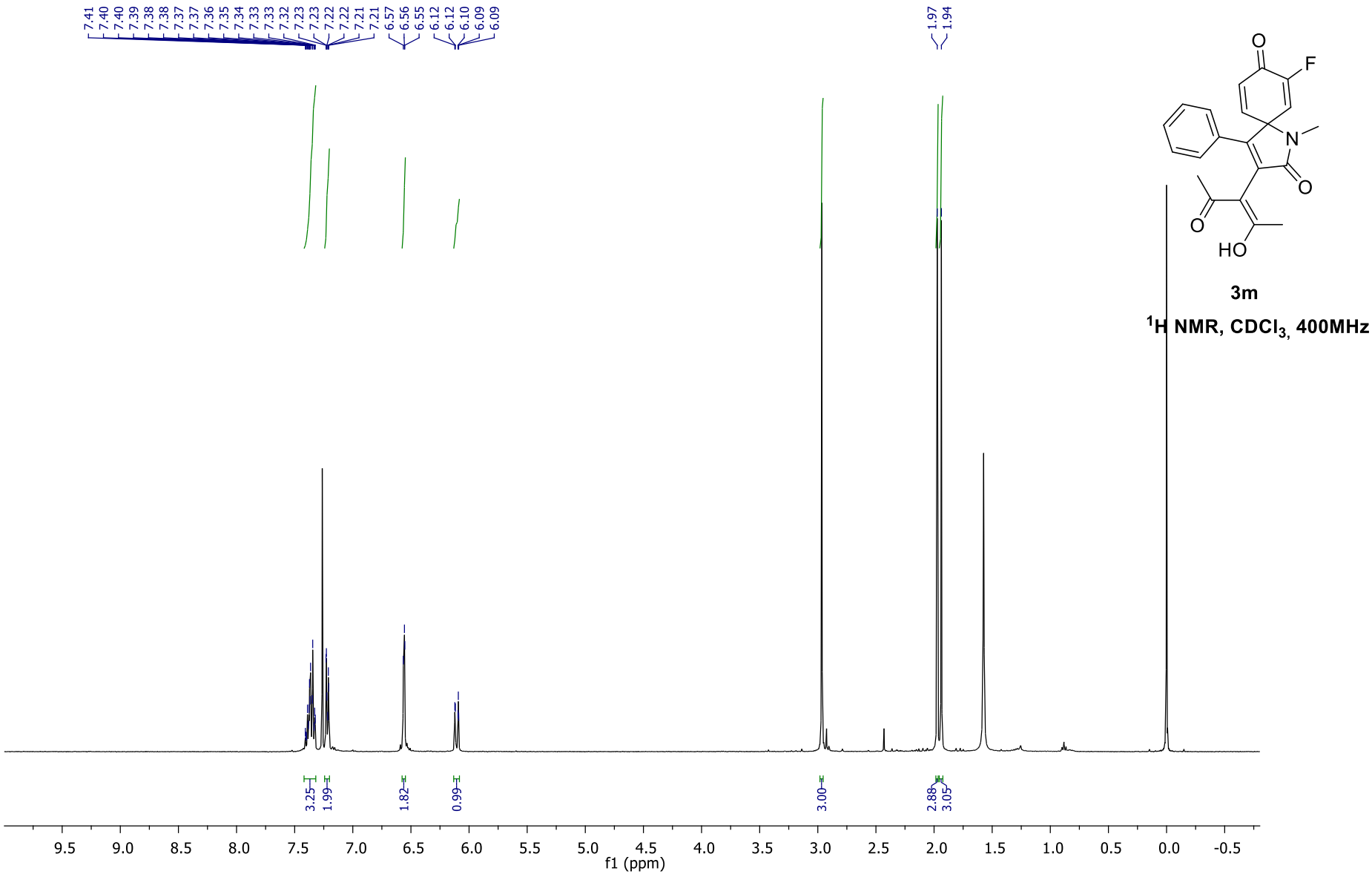
3l

^{1}H NMR, $CDCl_3$, 400MHz



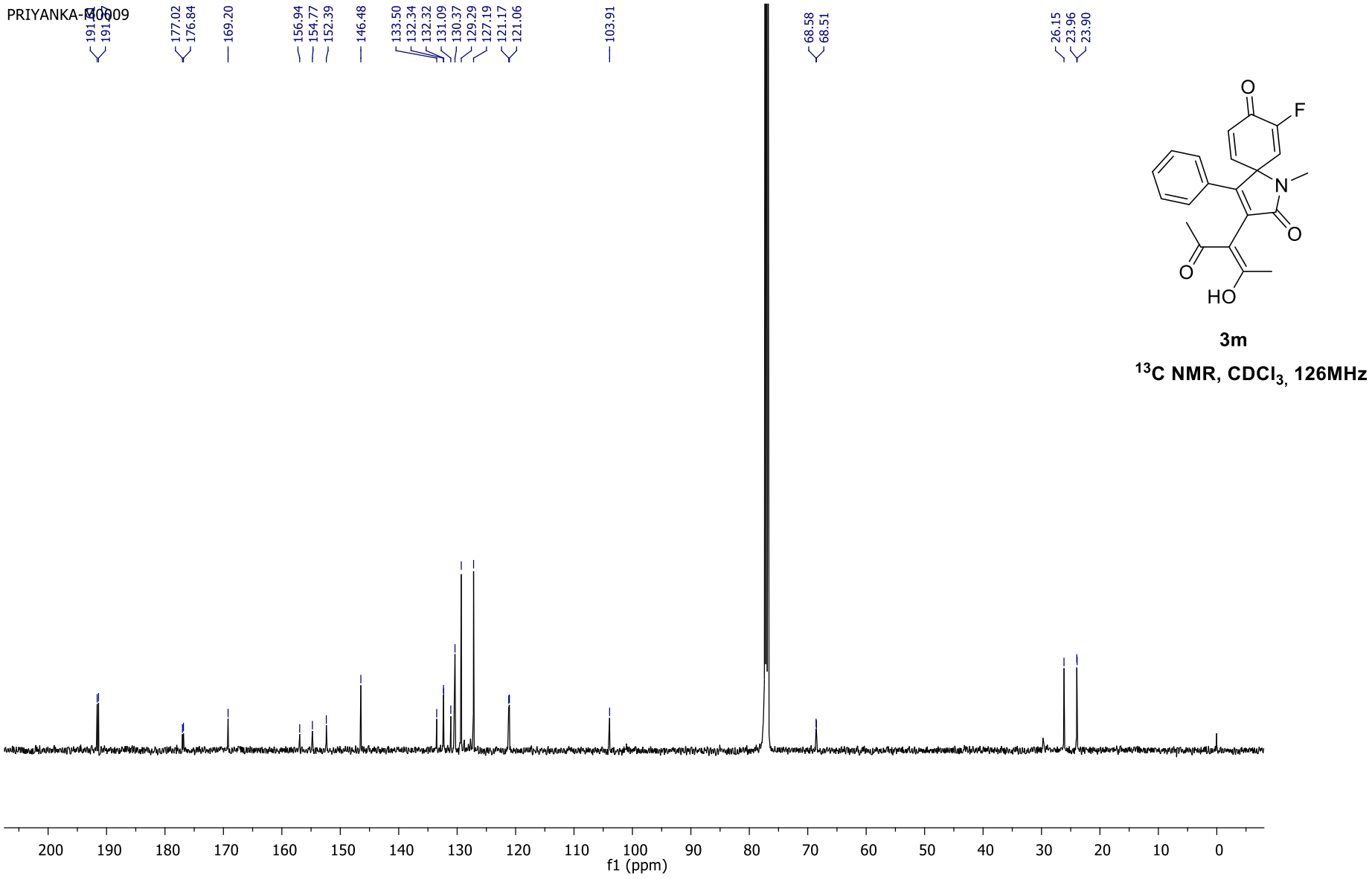
3l

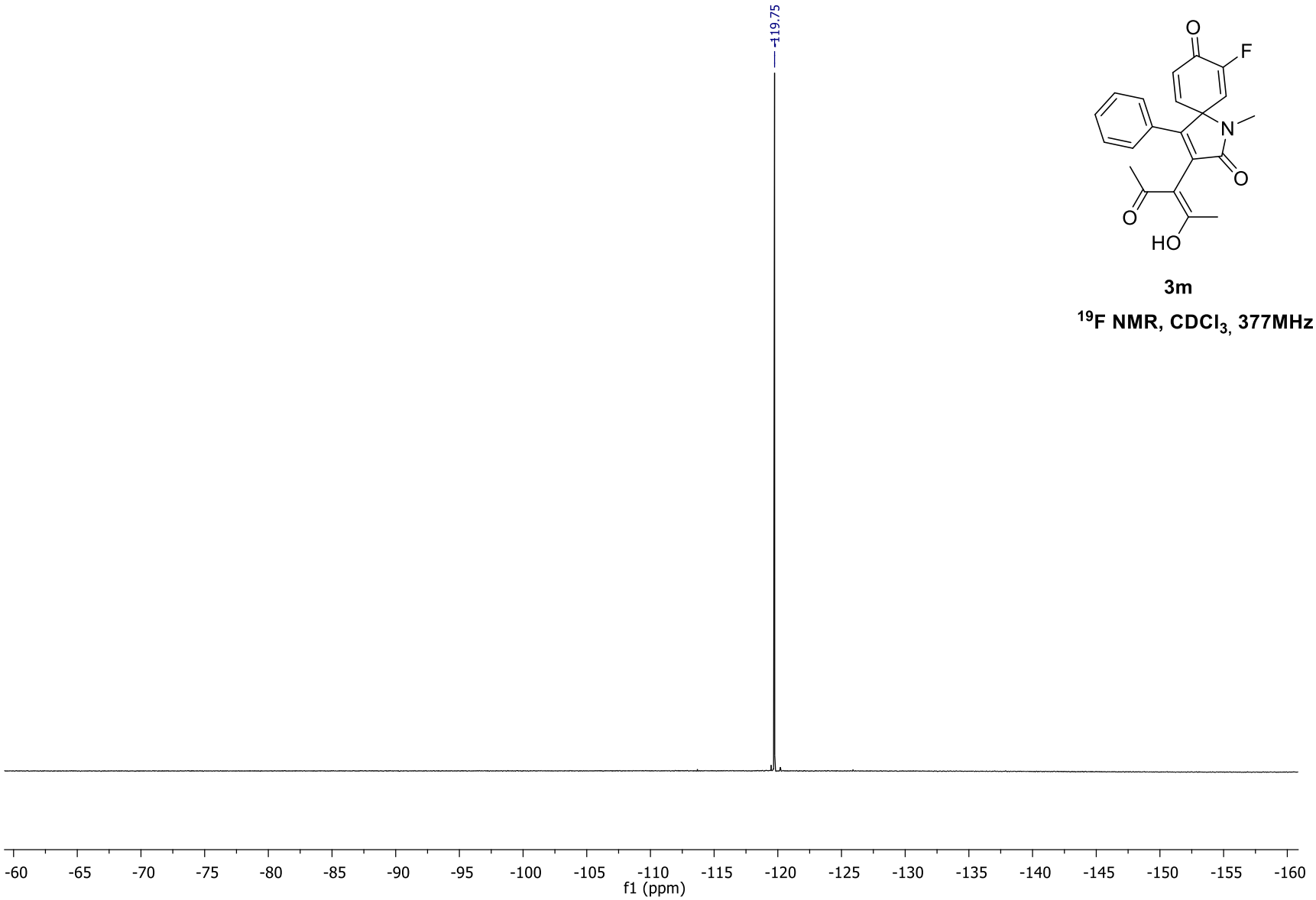
^{13}C NMR, $CDCl_3$, 101MHz



3m

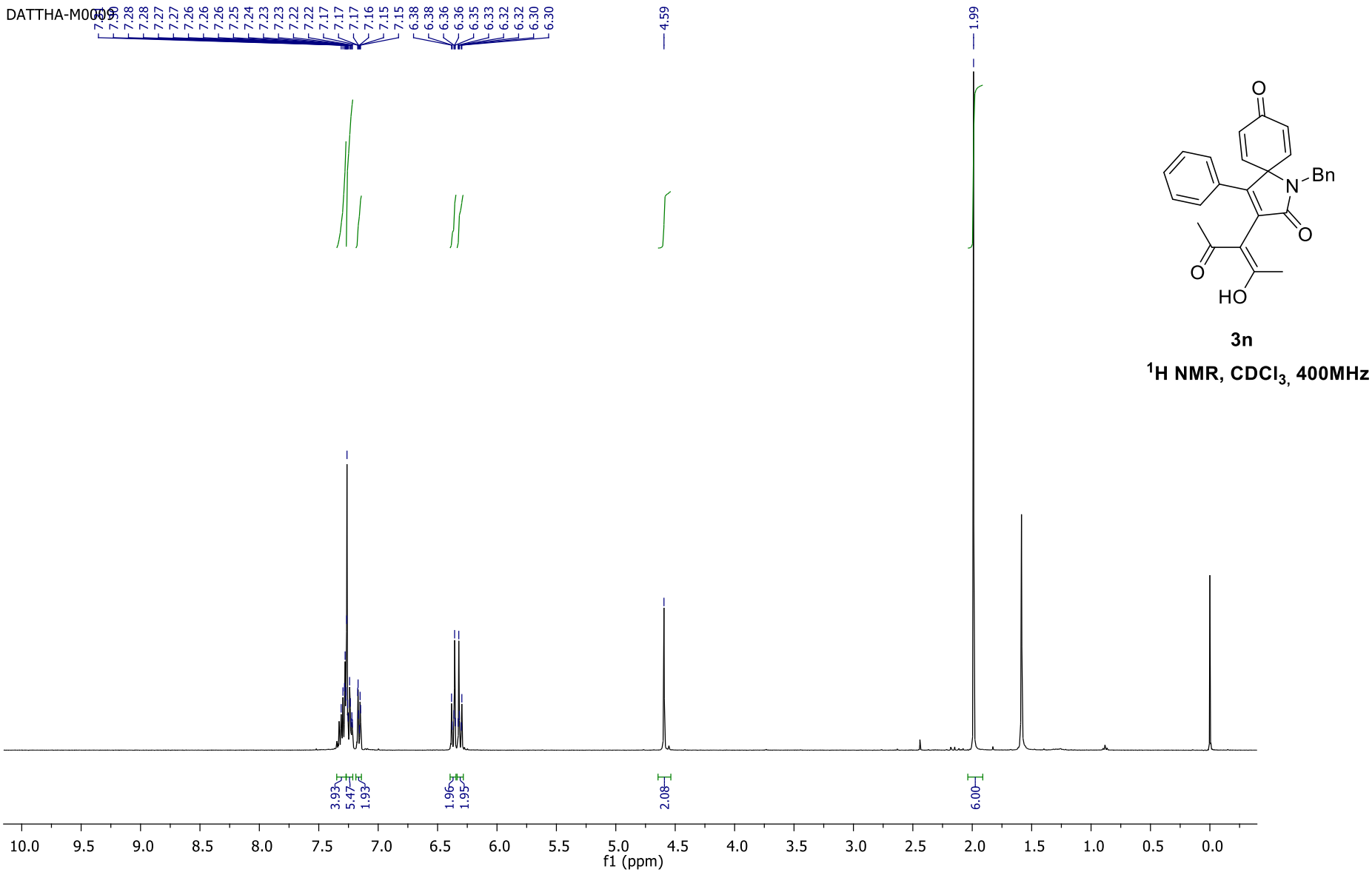
^{1}H NMR, $CDCl_3$, 400MHz


PRIYANKA-M0009
191.03
191.01
177.02
176.84
169.20
156.94
154.77
152.39
146.48
133.50
132.34
132.32
131.09
130.37
129.29
127.19
121.17
121.06
103.91
68.58
68.51
26.15
23.96
23.90
O
F
N
O
O
HO
3m
^{13}C NMR, CDCl$_3$, 126MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



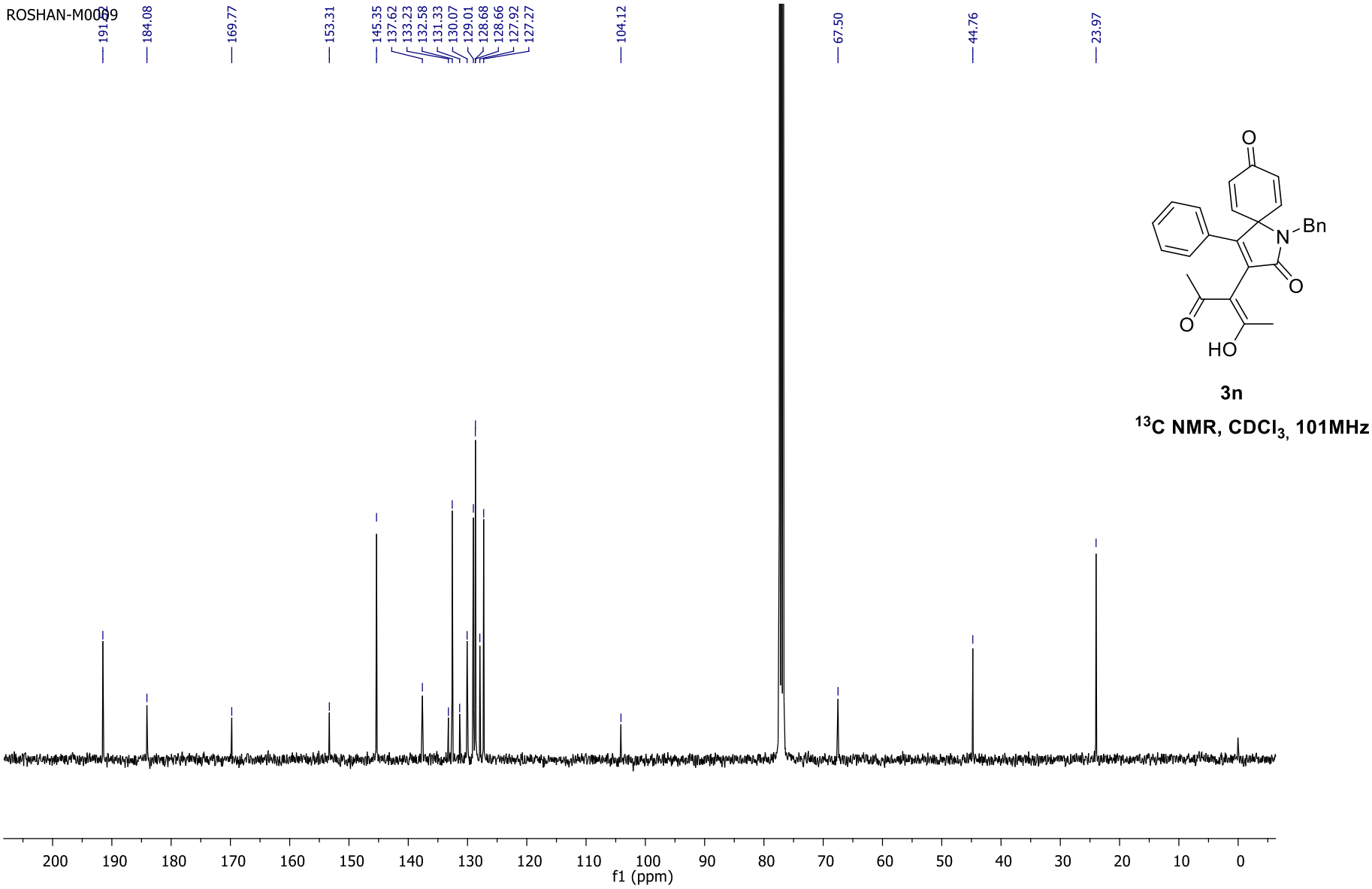
3m

^{19}F NMR, $CDCl_3$, 377MHz



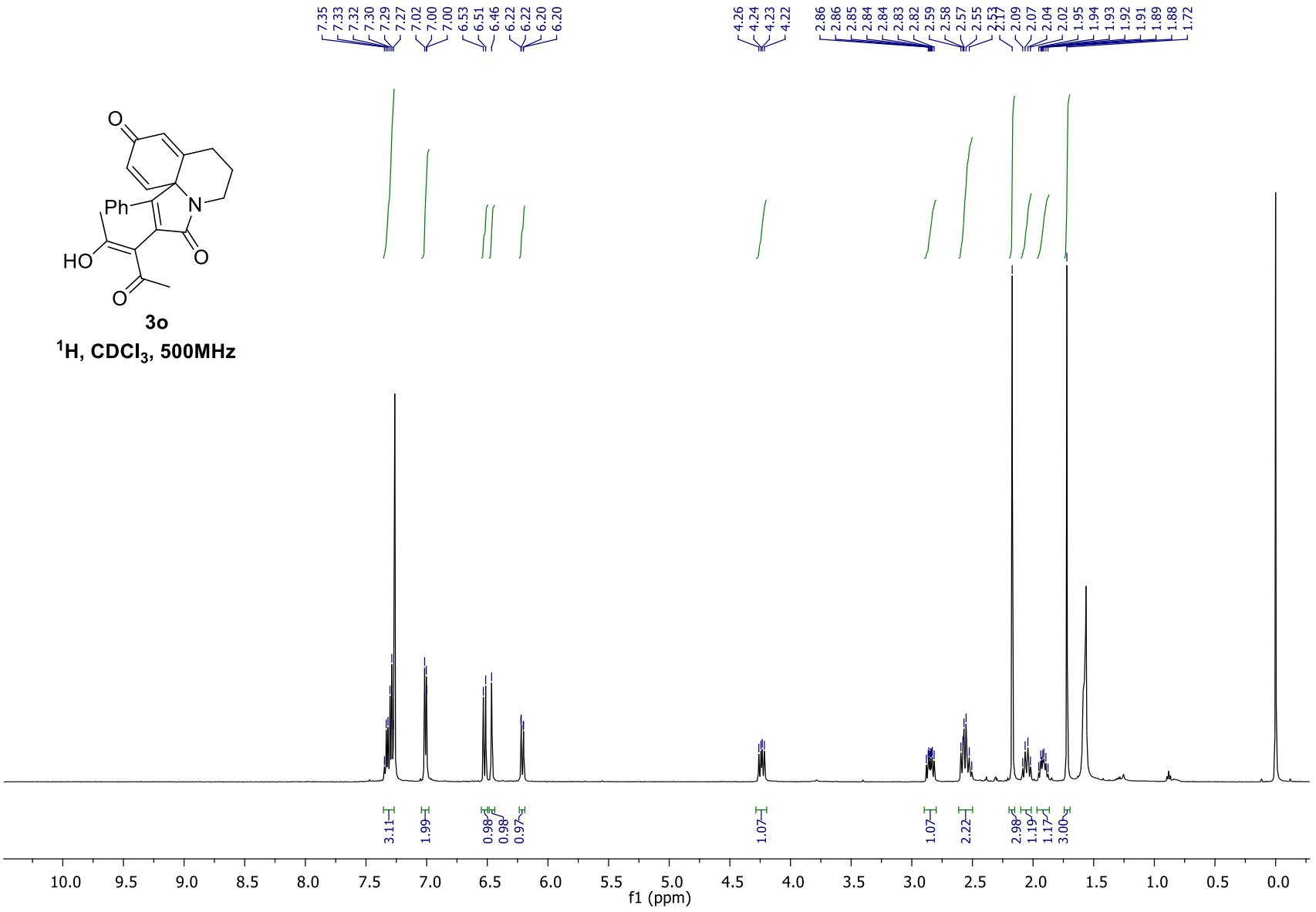
3n

^{1}H NMR, $CDCl_3$, 400MHz



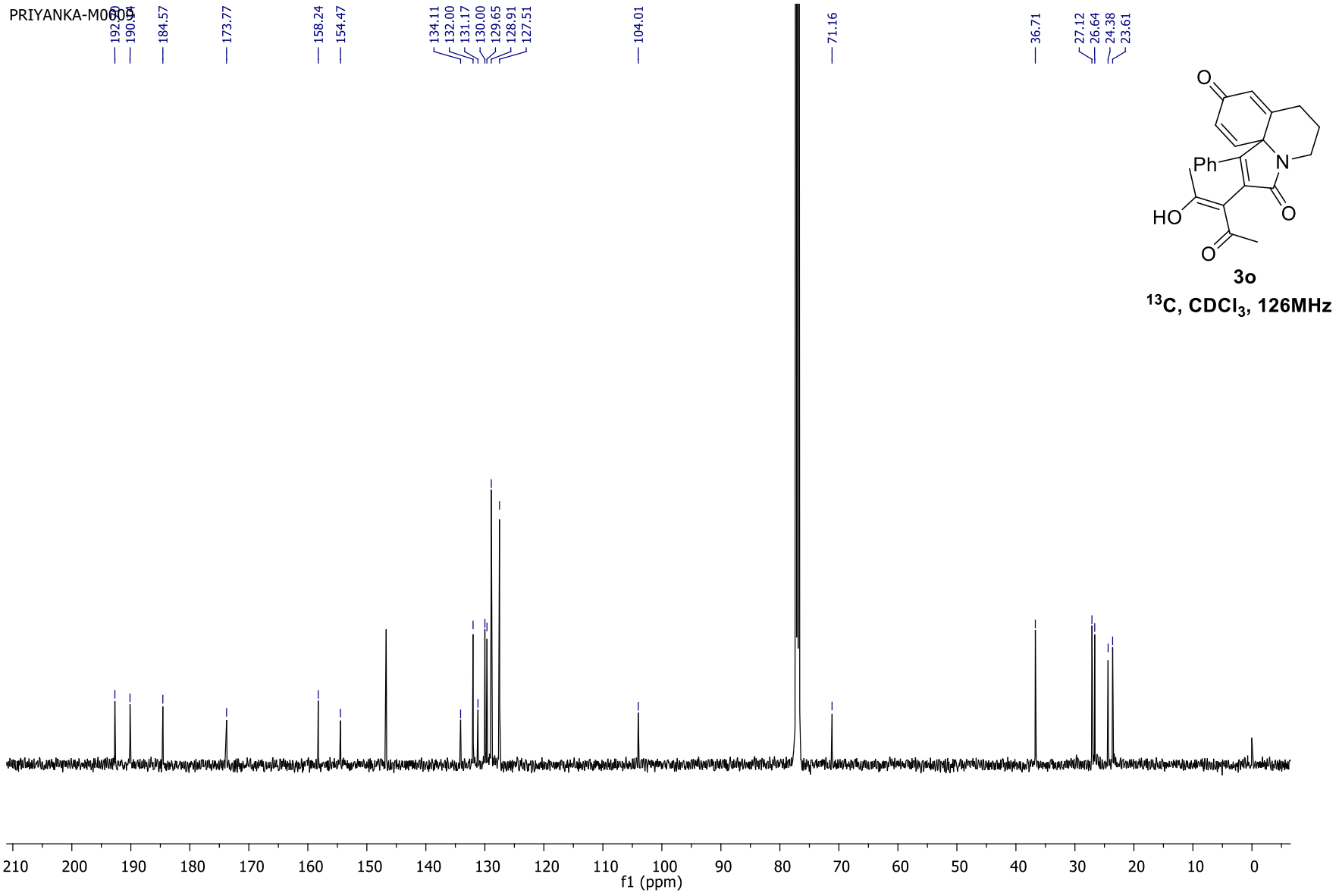
3n

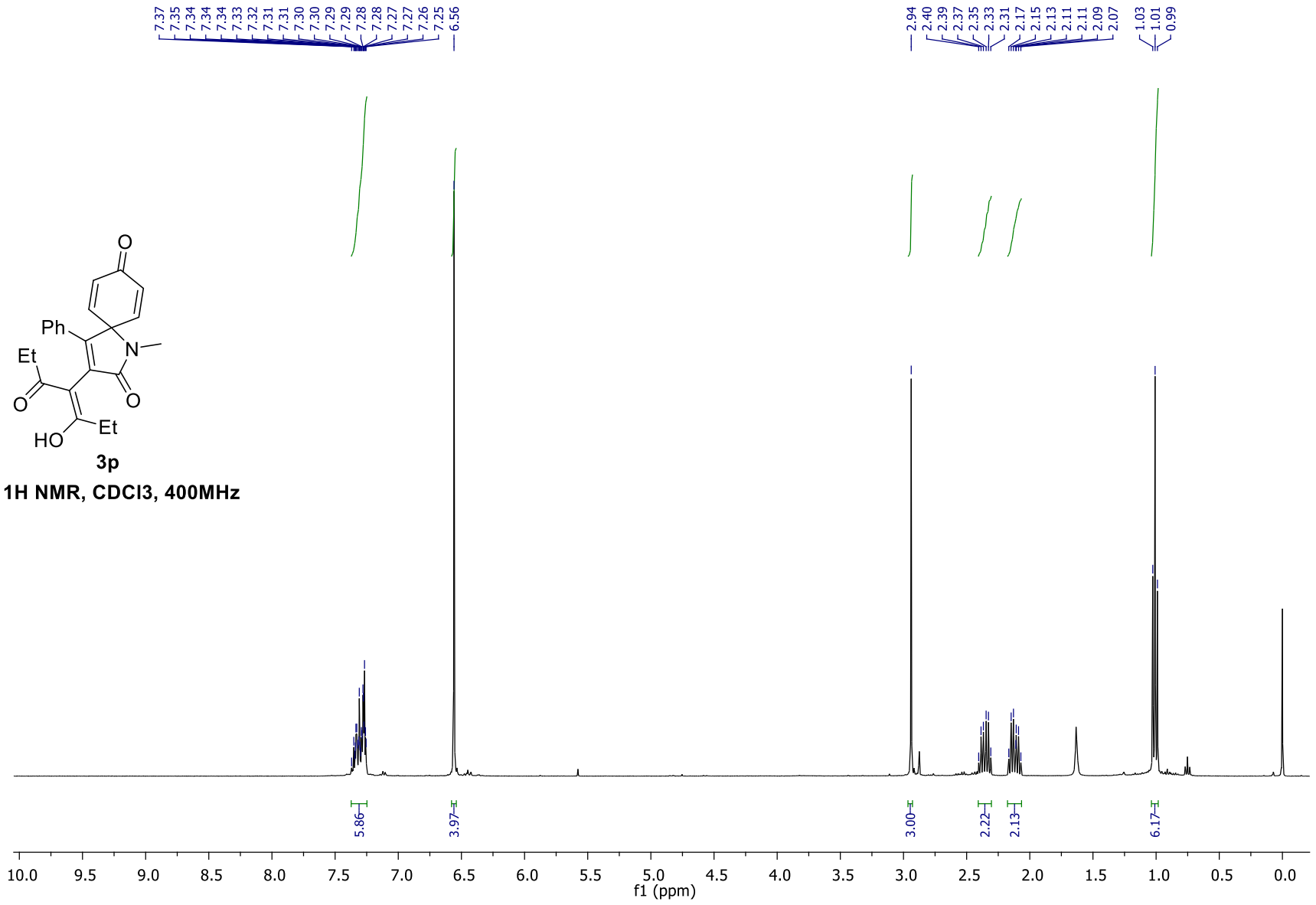
^{13}C NMR, $CDCl_3$, 101MHz



3o

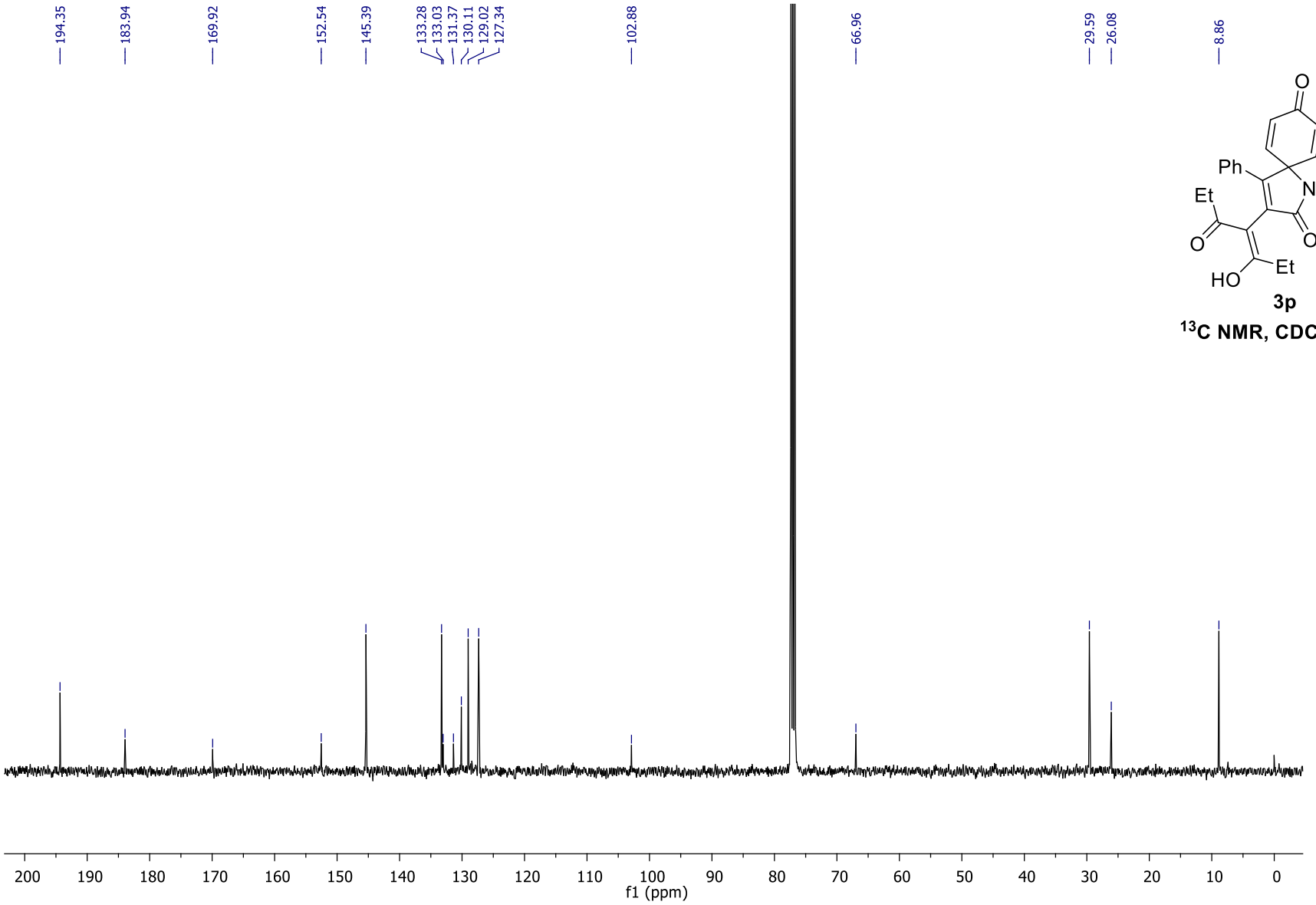
^{1}H, $CDCl_3$, 500MHz


PRIYANKA-M0605
192.03
190.44
184.57
173.77
158.24
154.47
134.11
132.00
131.17
130.00
129.65
128.91
127.51
104.01
71.16
36.71
27.12
26.64
24.38
23.61
O
Ph
N
HO
O
O
3o
13C, CDCl3, 126MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



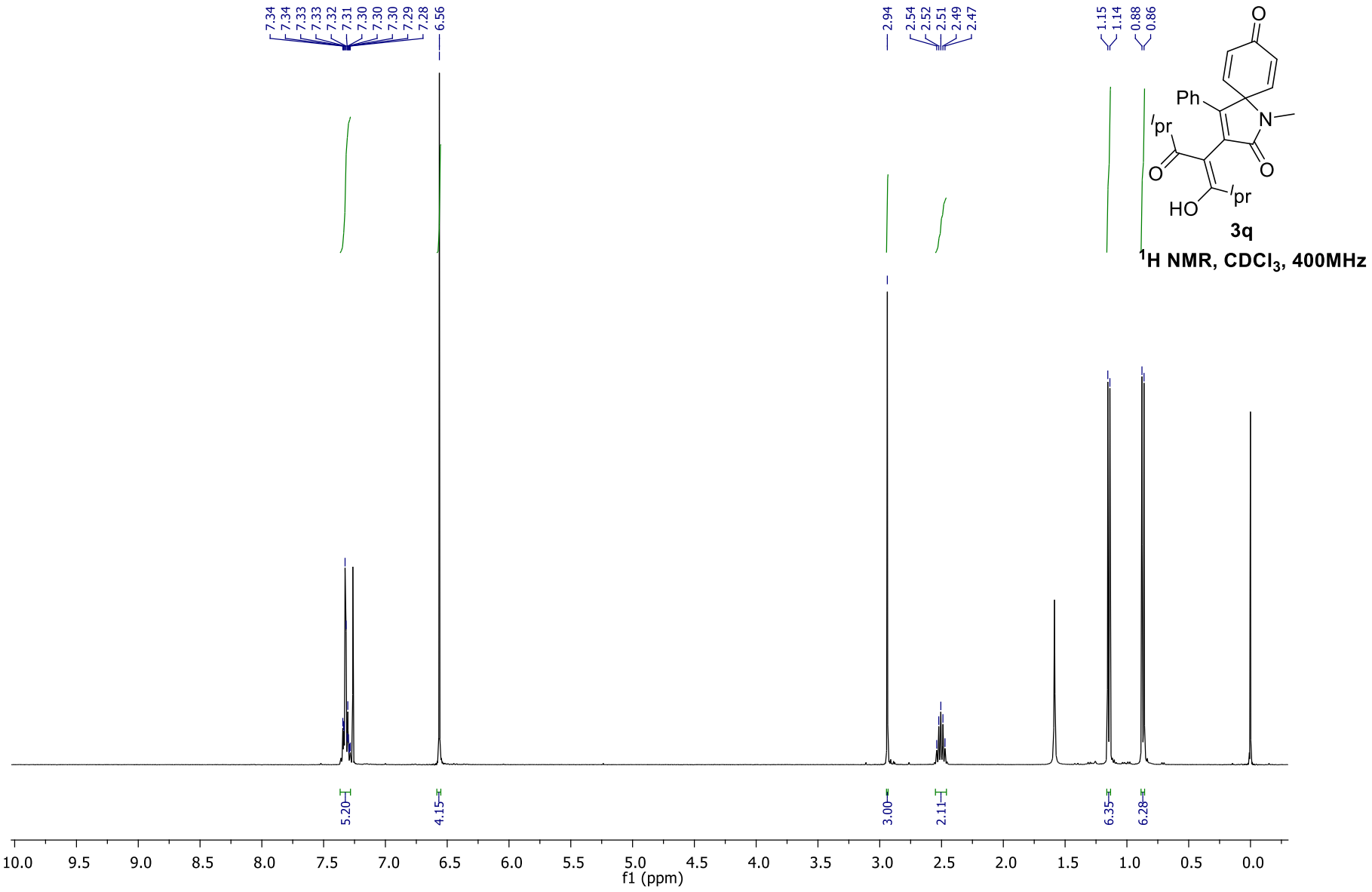
3p

1H NMR, CDCl3, 400MHz



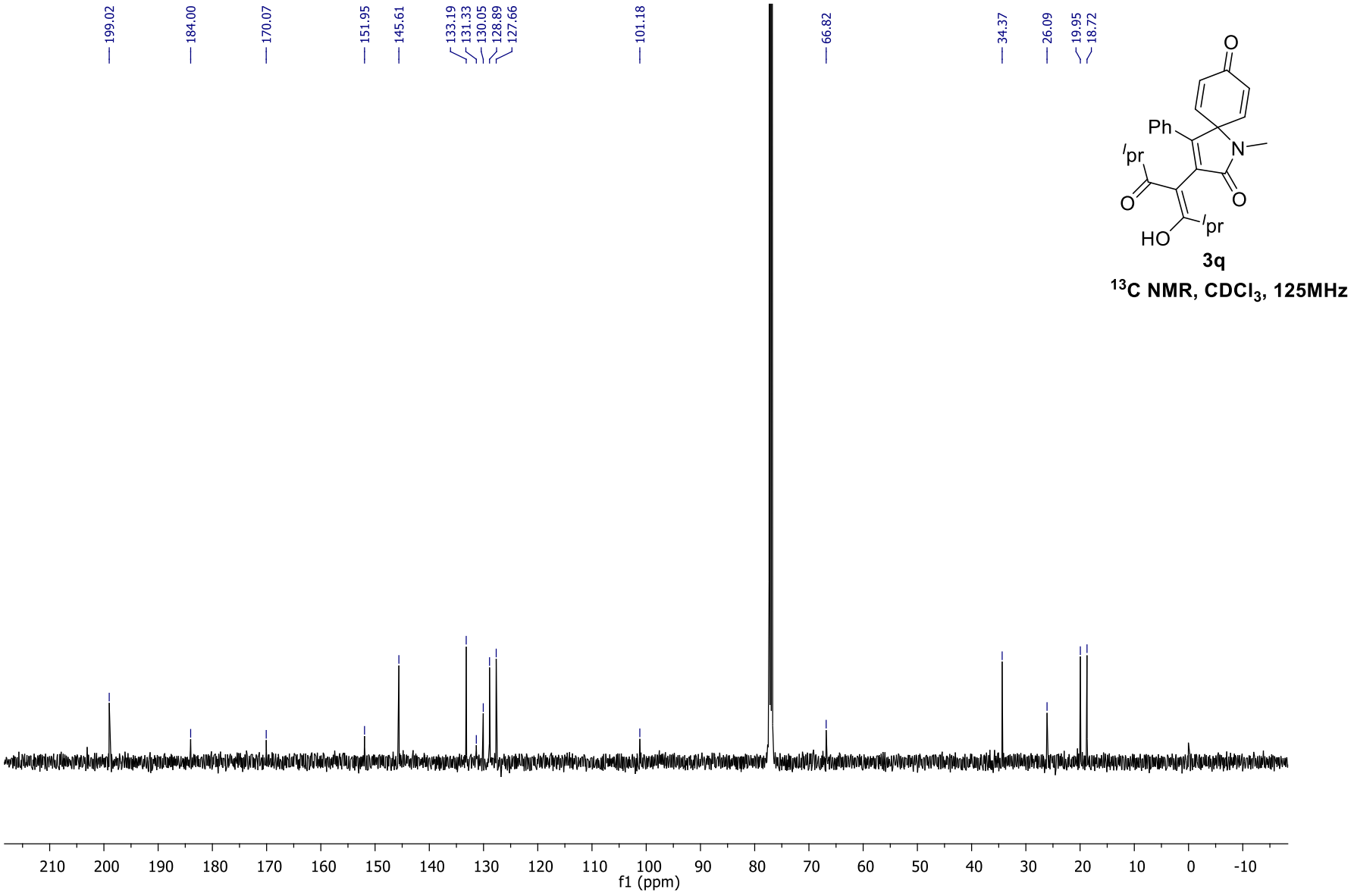
3p

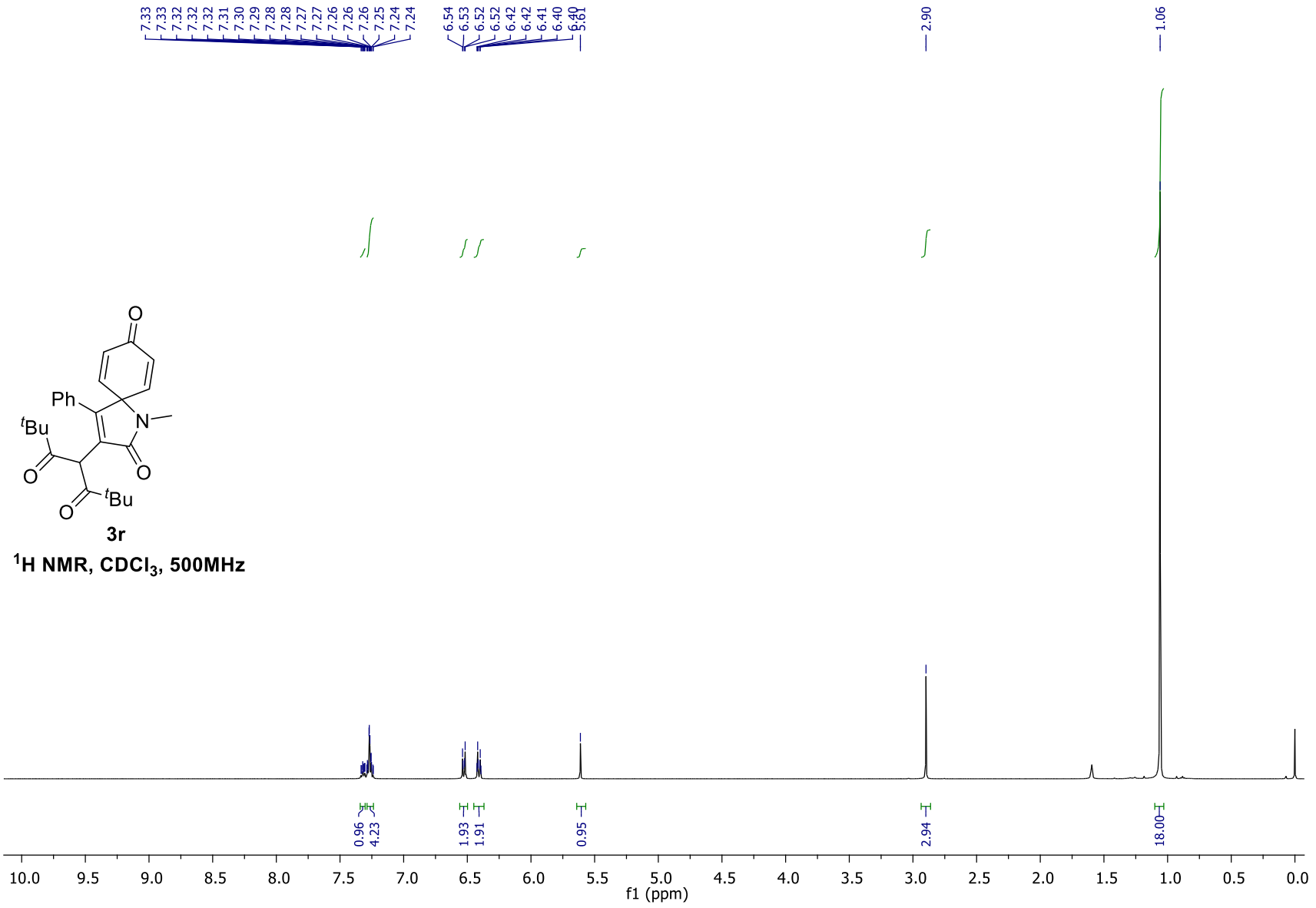
^{13}C NMR, $CDCl_3$, 101MHz



3q

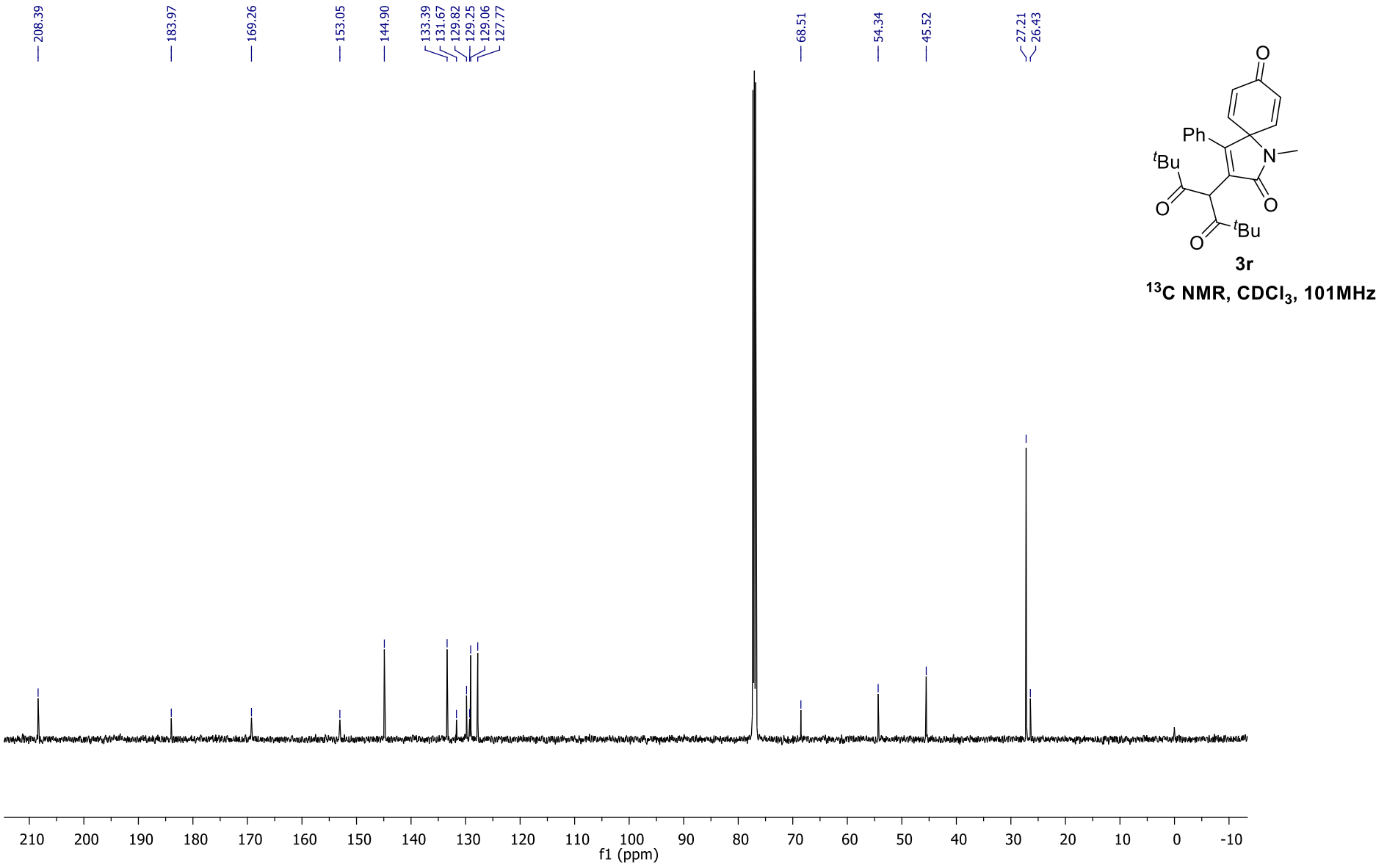
^{1}H NMR, $CDCl_3$, 400MHz

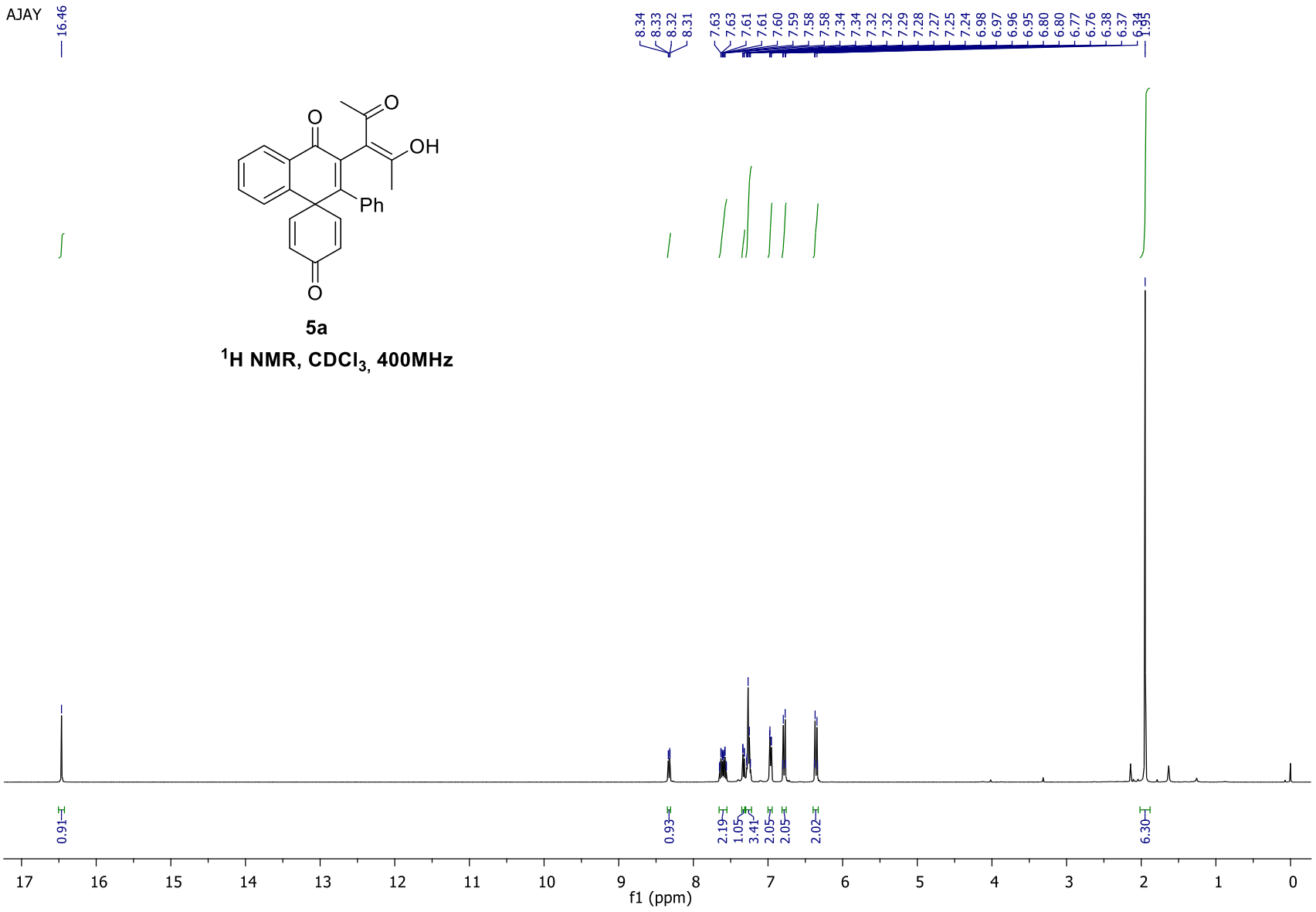

199.02
184.00
170.07
151.95
145.61
133.19
131.33
130.05
128.89
127.66
101.18
66.82
34.37
26.09
19.95
18.72
O
Ph
N
iPr
O
O
O
HO
iPr
3q
13C NMR, CDCl3, 125MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3r

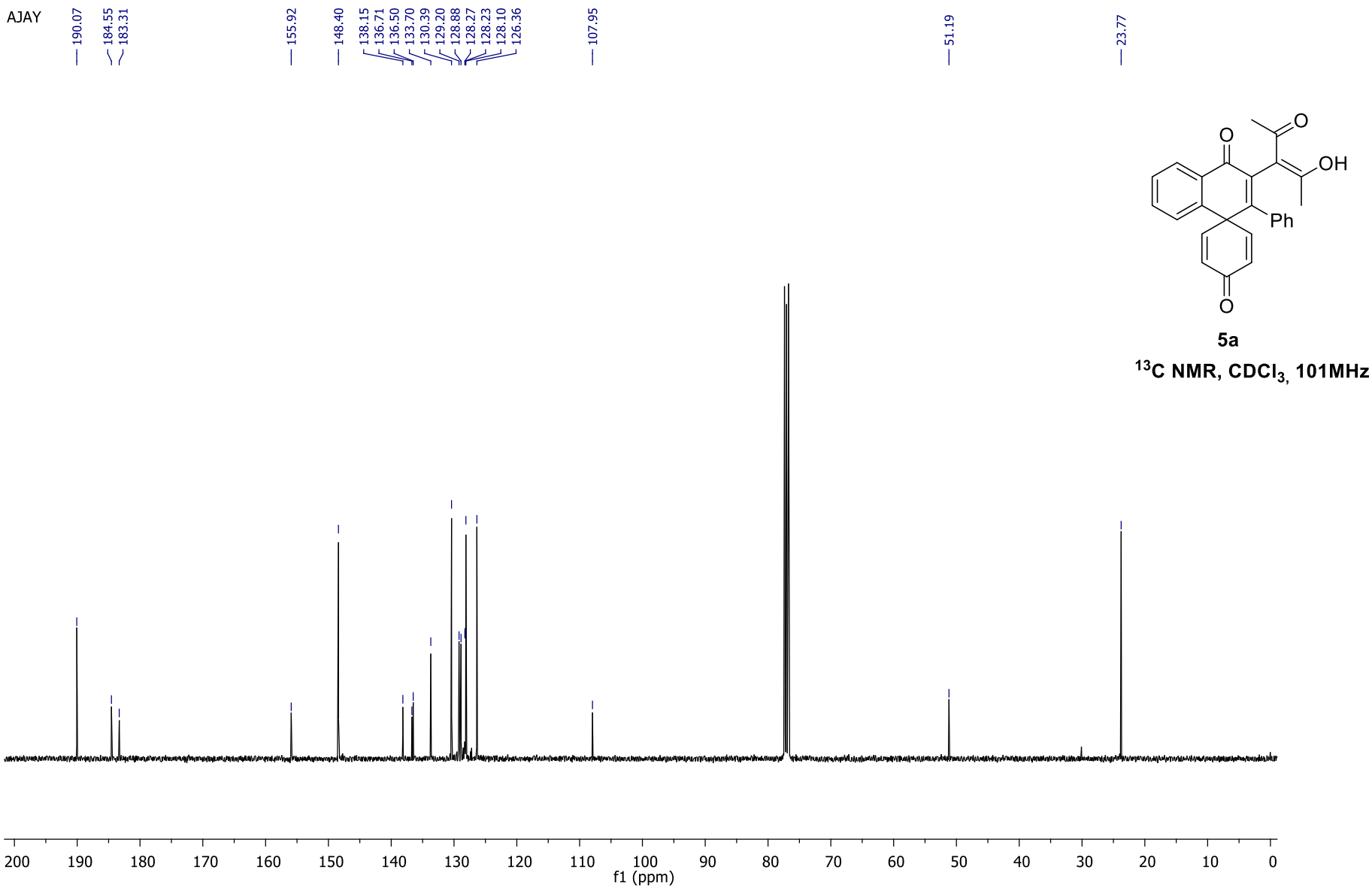
^{1}H NMR, $CDCl_3$, 500MHz

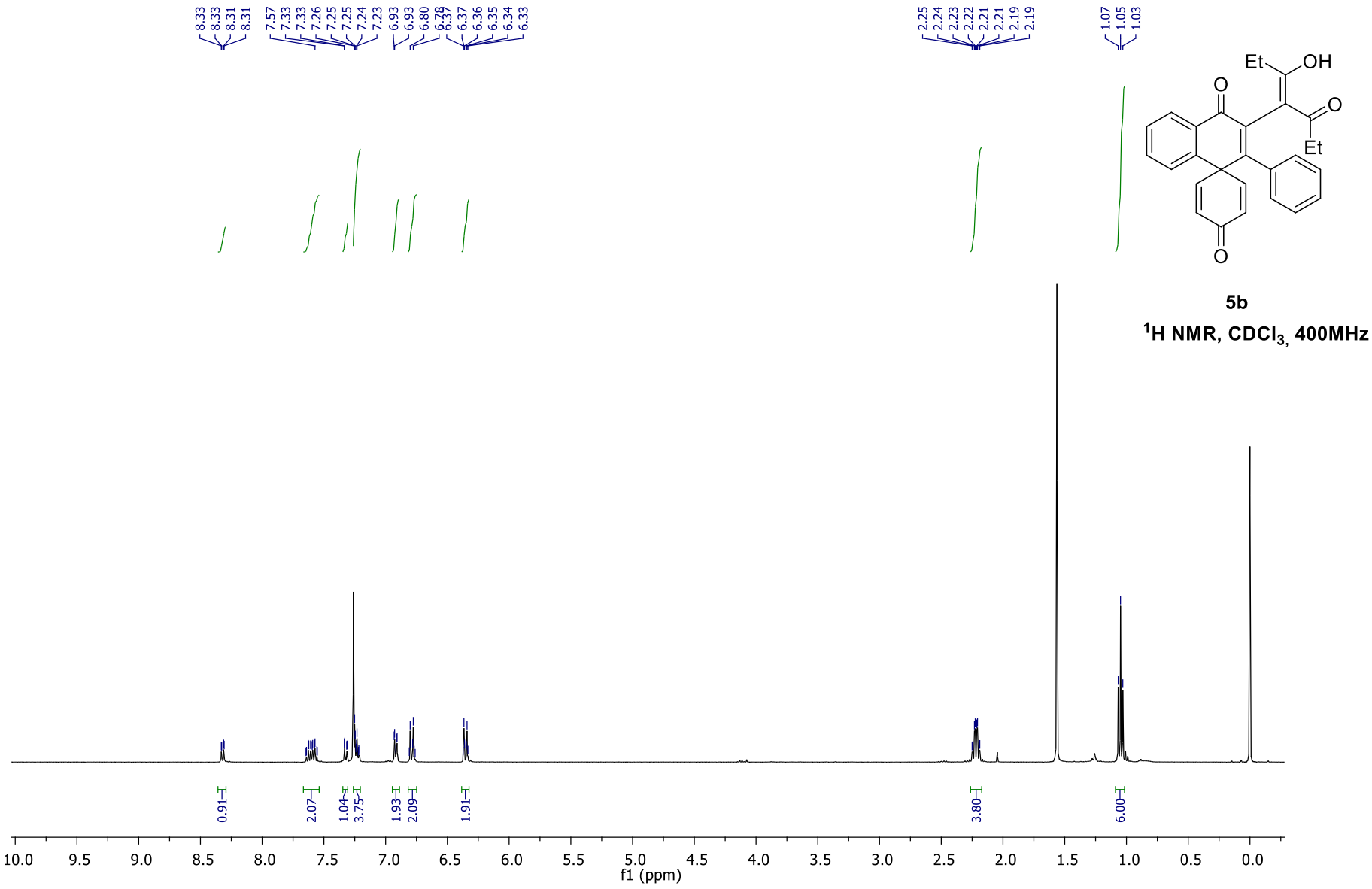

208.39
183.97
169.26
153.05
144.90
133.39
131.67
129.82
129.25
129.06
127.77
68.51
54.34
45.52
27.21
26.43
O
Ph
N
tBu
O
O
O
tBu
3r
13C NMR, CDCl3, 101MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5a

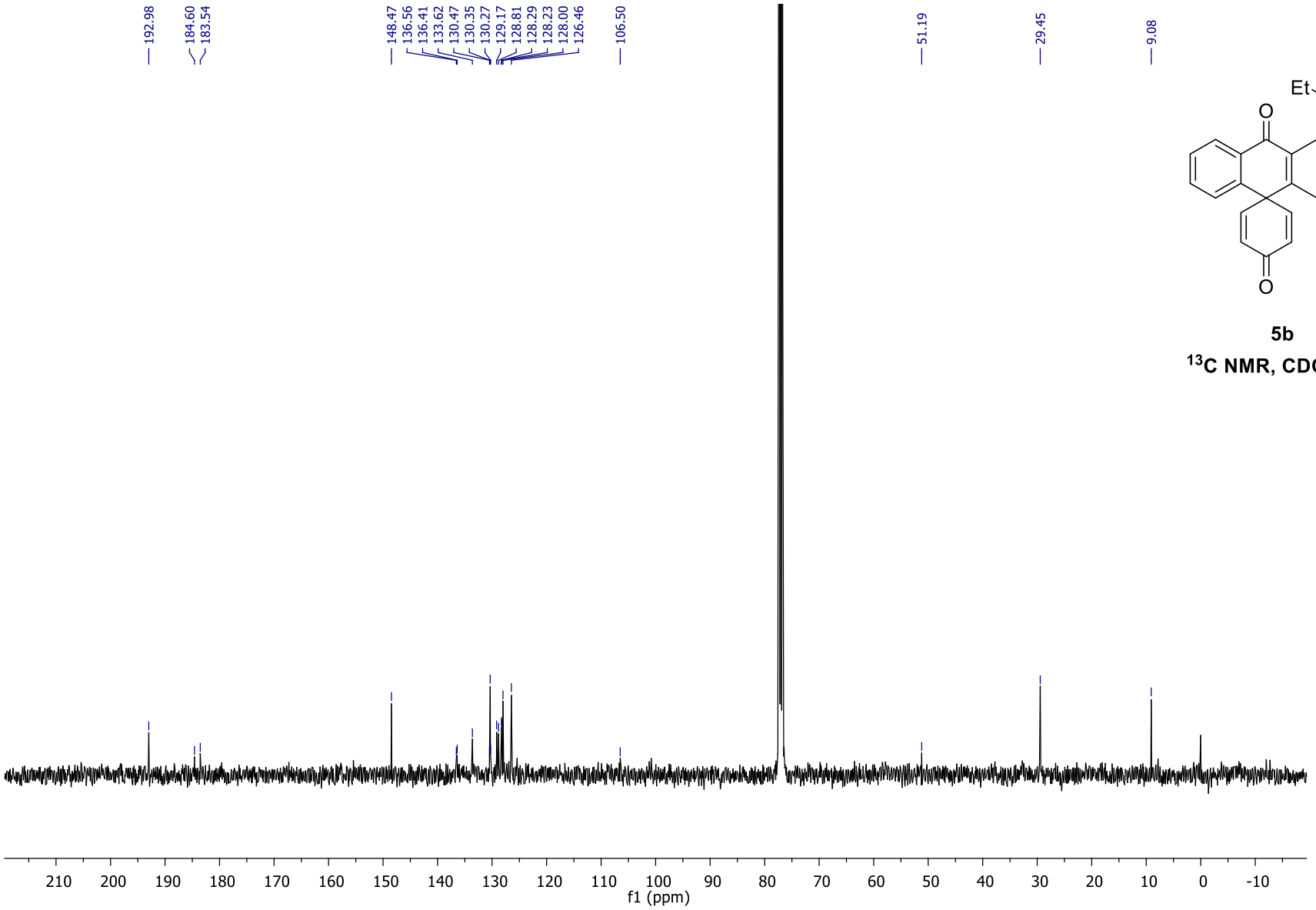
^{1}H NMR, $CDCl_3$, 400MHz


AJAY
190.07
184.55
183.31
155.92
148.40
138.15
136.71
136.50
133.70
130.39
129.20
128.88
128.27
128.23
128.10
126.36
107.95
51.19
23.77
O
O
OH
Ph
O
5a
13C NMR, CDCl3, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



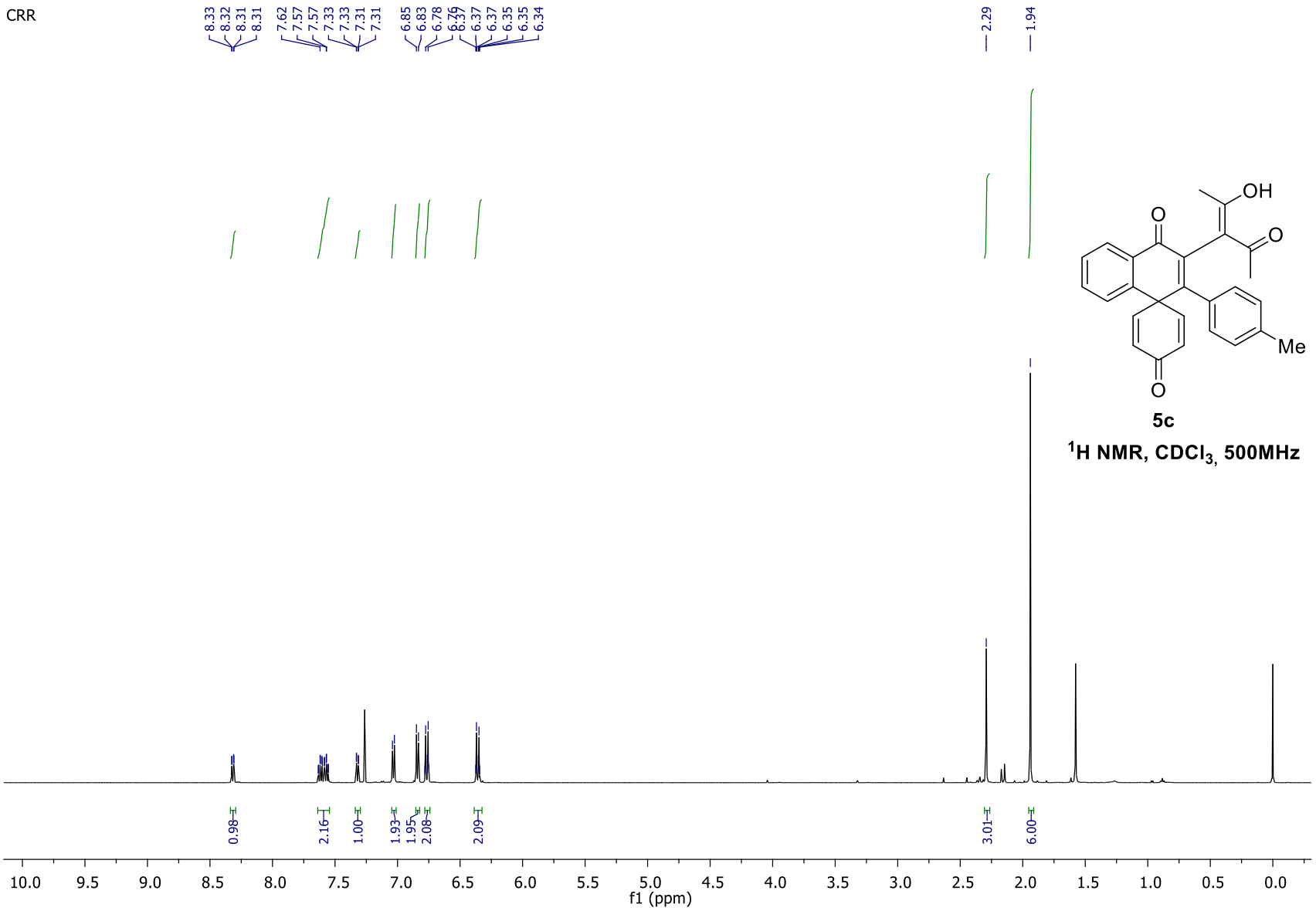
5b

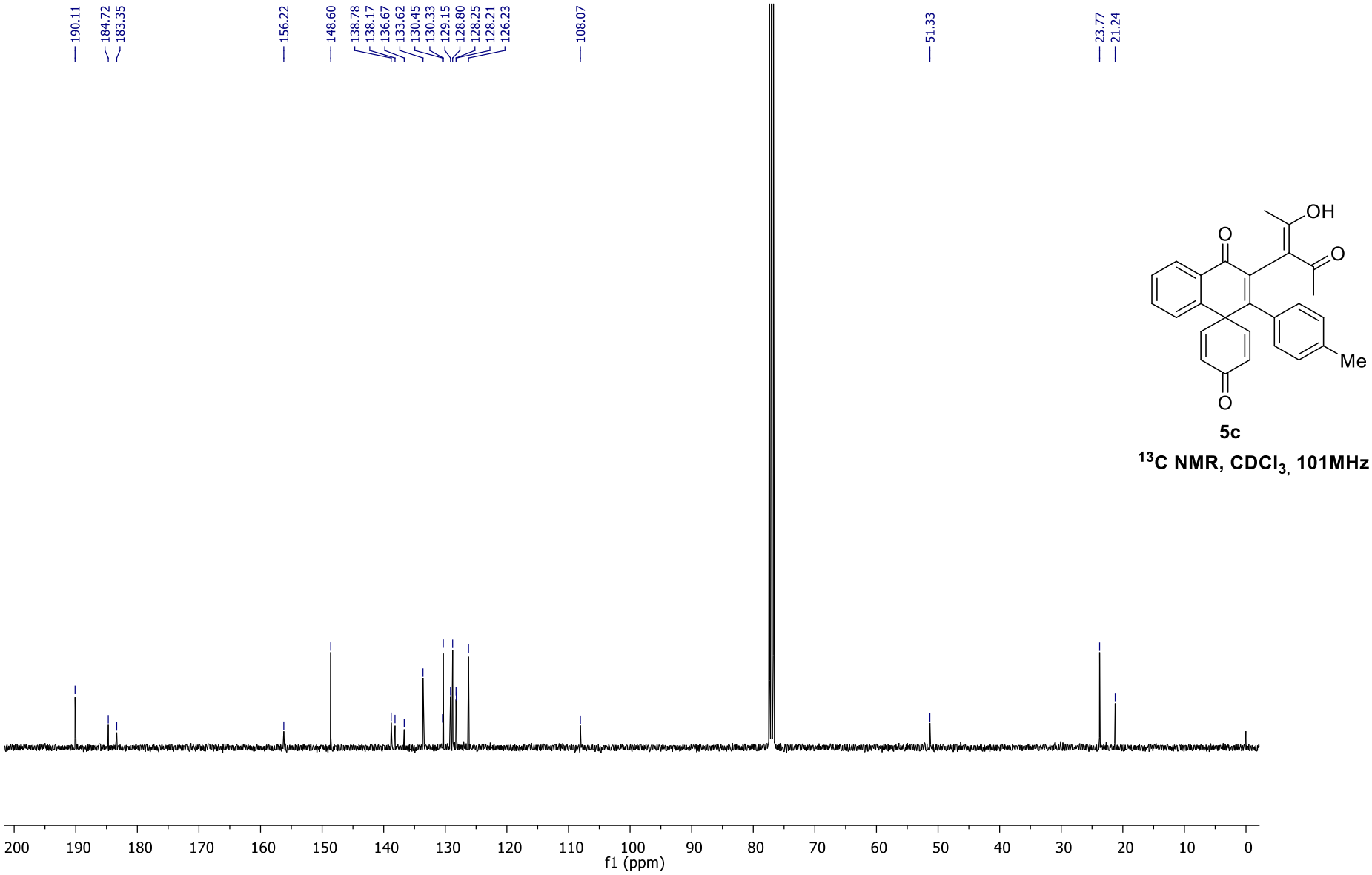
^{1}H NMR, $CDCl_3$, 400MHz



5b

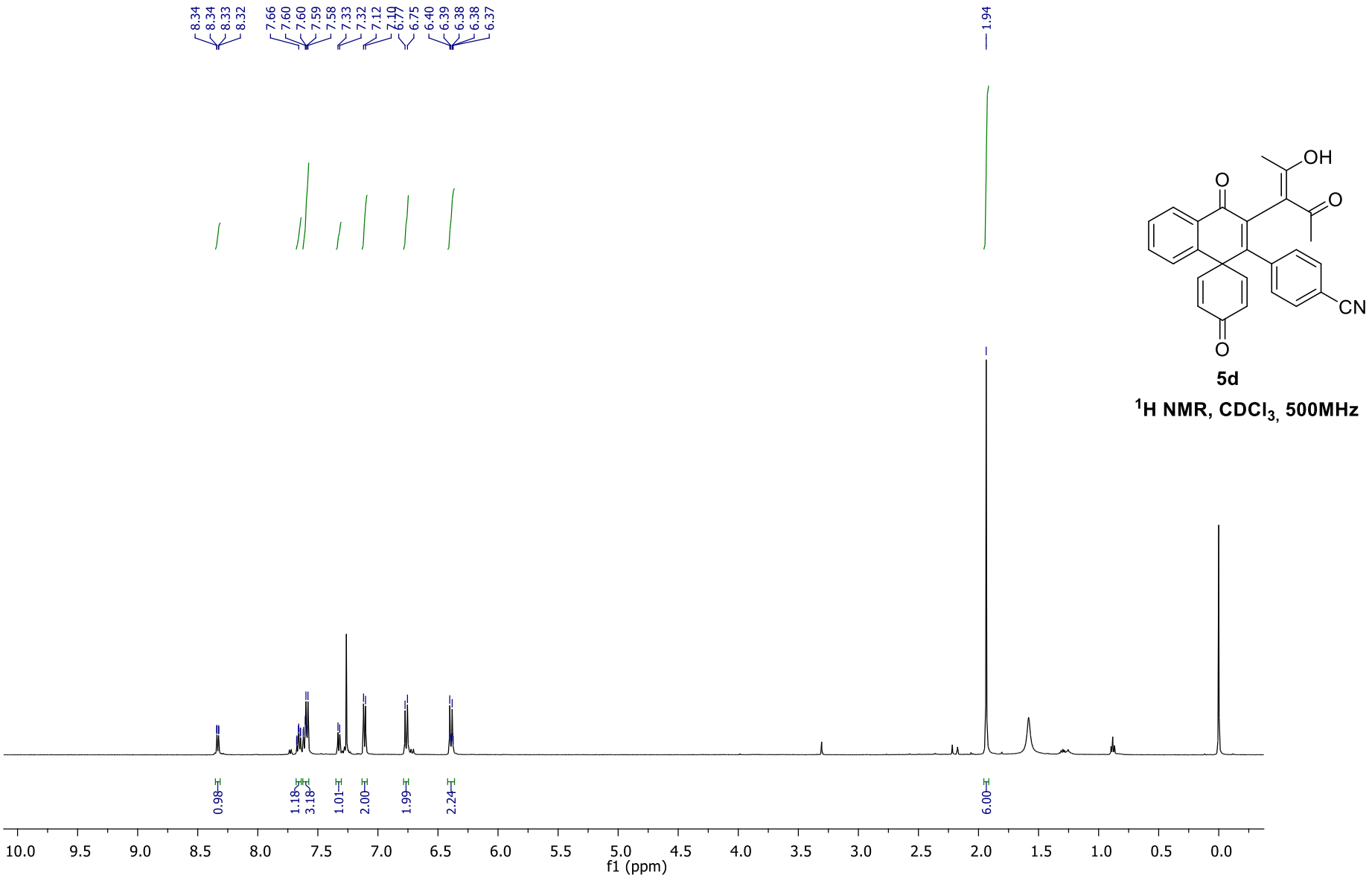
^{13}C NMR, $CDCl_3$, 101MHz


CRR
8.33
8.32
8.31
8.31
7.62
7.57
7.57
7.33
7.33
7.31
7.31
6.85
6.83
6.78
6.37
6.37
6.35
6.35
6.34
2.29
1.94
OH
O
O
O
Me
5c
^{1}H NMR, CDCl$_3$, 500MHz
0.98
2.16
1.00
1.93
1.95
2.08
2.09
3.01
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



5c

^{13}C NMR, $CDCl_3$, 101MHz

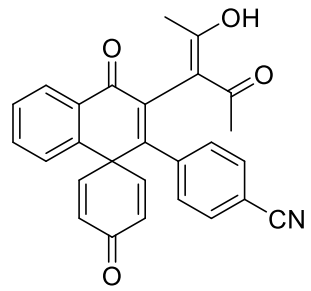


5d

^{1}H NMR, $CDCl_3$, 500MHz

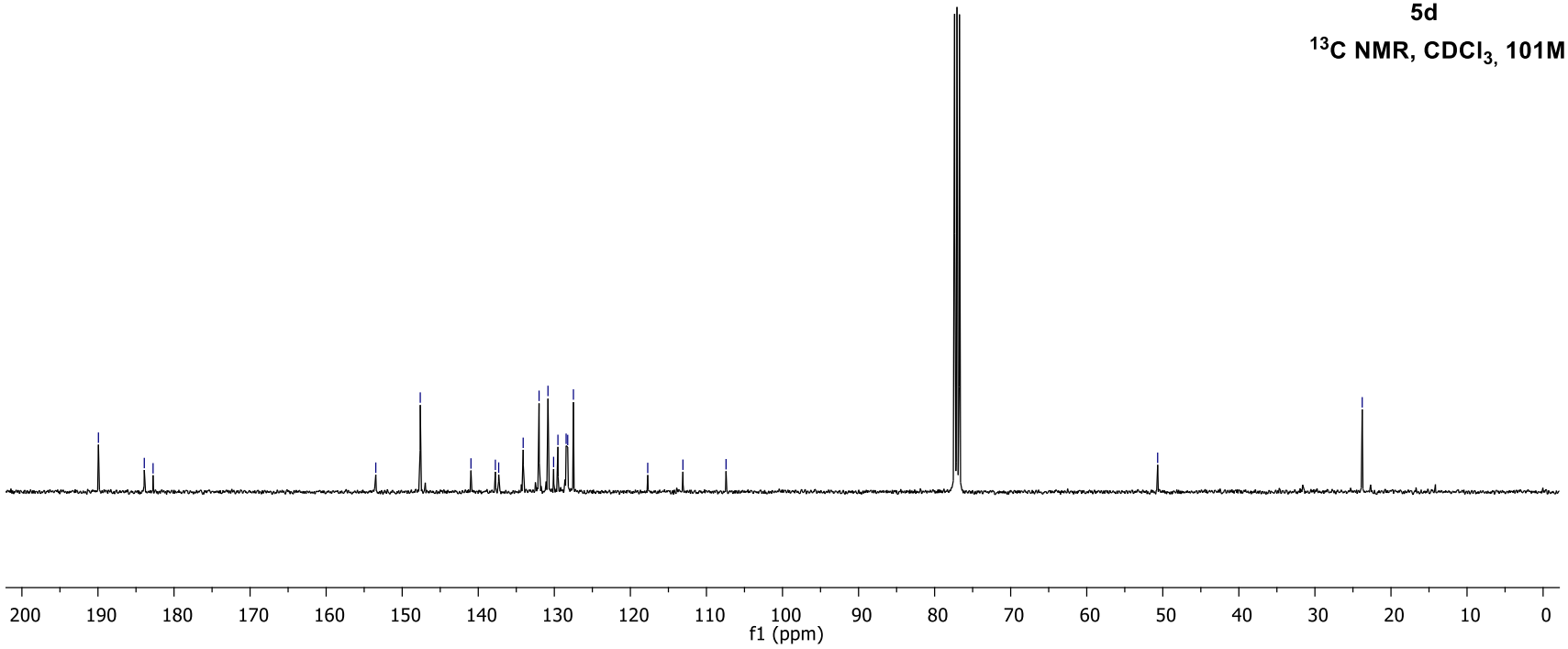
AJAY
OSPC1886

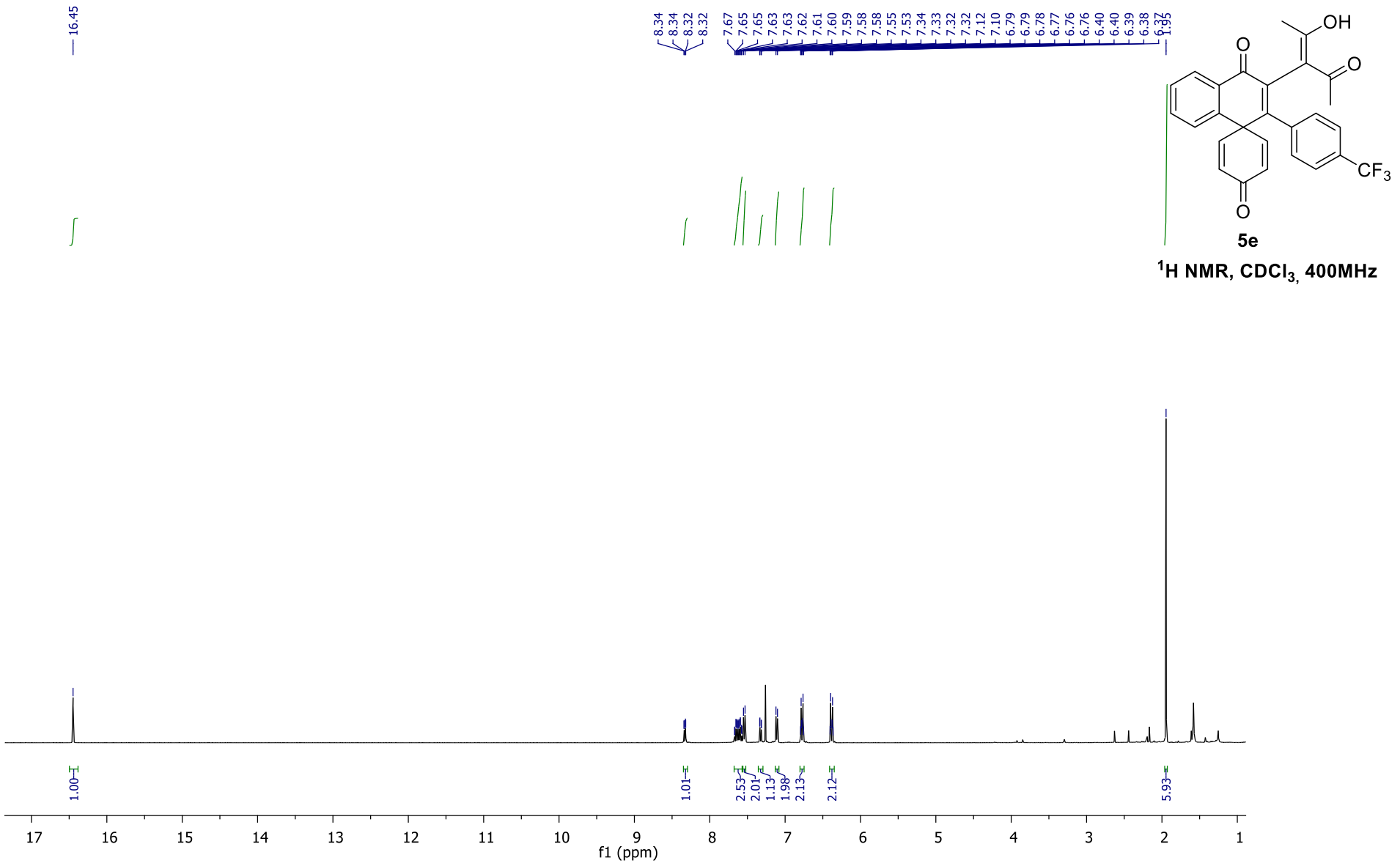
189.94
183.91
182.75
153.47
147.62
140.96
137.75
137.31
134.09
132.00
130.83
130.09
129.53
128.45
128.24
127.49
117.72
113.09
107.42
50.68
23.78

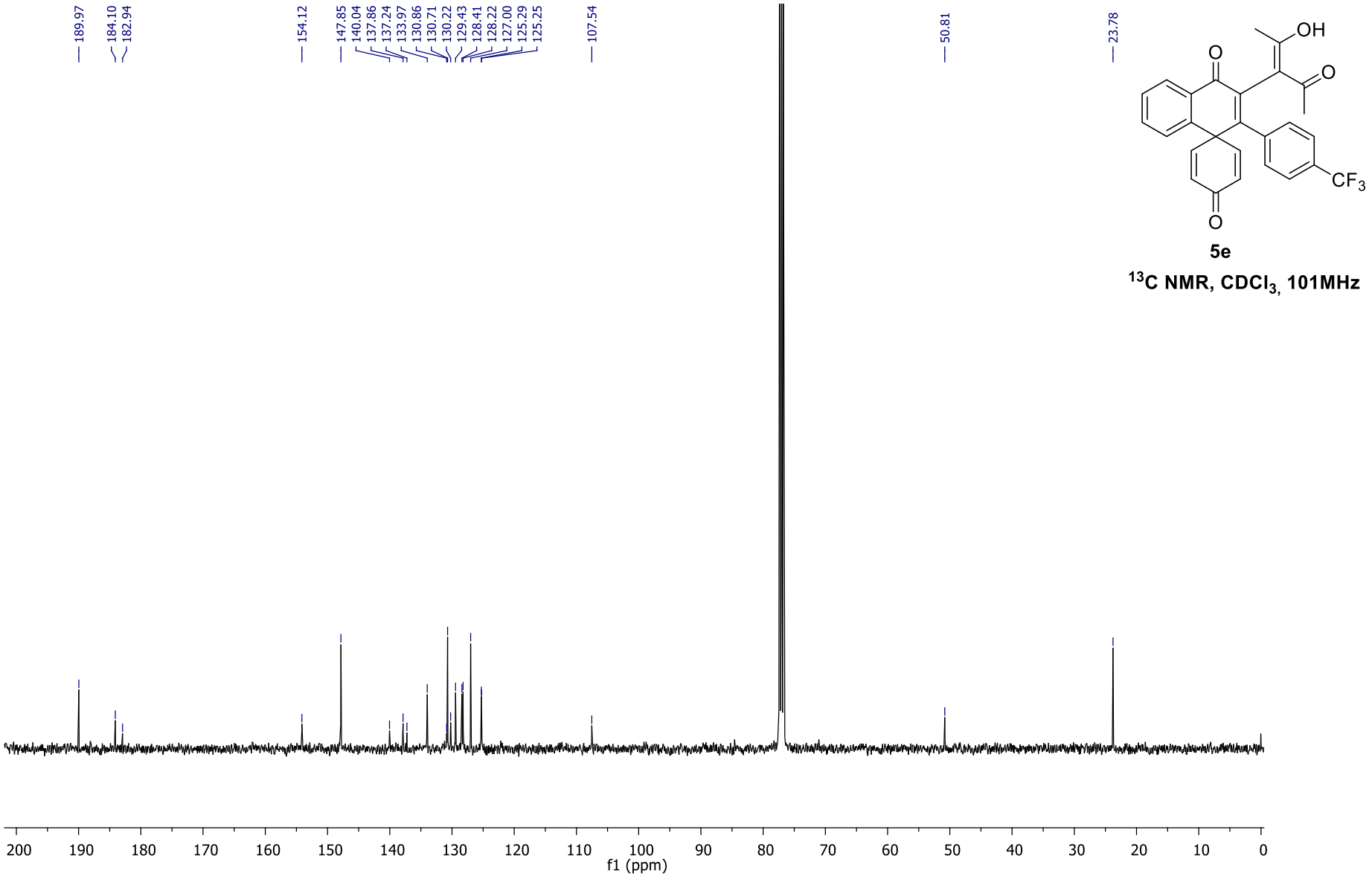


5d

^{13}C NMR, $CDCl_3$, 101MHz

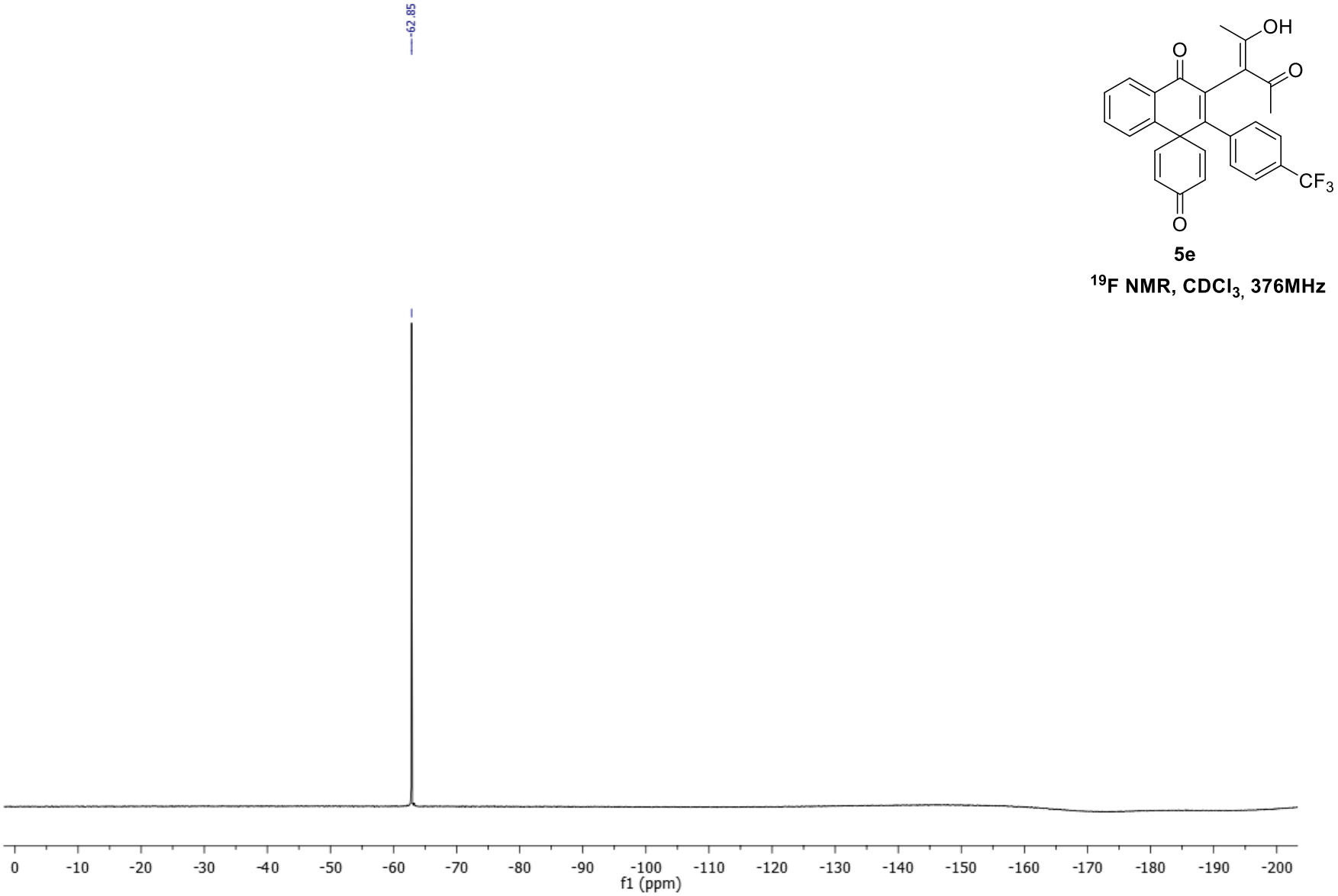



16.45
8.34
8.34
8.32
8.32
7.67
7.65
7.65
7.63
7.63
7.62
7.61
7.60
7.59
7.58
7.58
7.55
7.53
7.34
7.33
7.32
7.32
7.12
7.10
6.79
6.79
6.78
6.77
6.76
6.76
6.40
6.40
6.39
6.38
1.95
OH
O
O
O
CF3
5e
1H NMR, CDCl3, 400MHz
1.00
1.01
2.53
2.01
1.13
1.98
2.13
2.12
5.93
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
f1 (ppm)



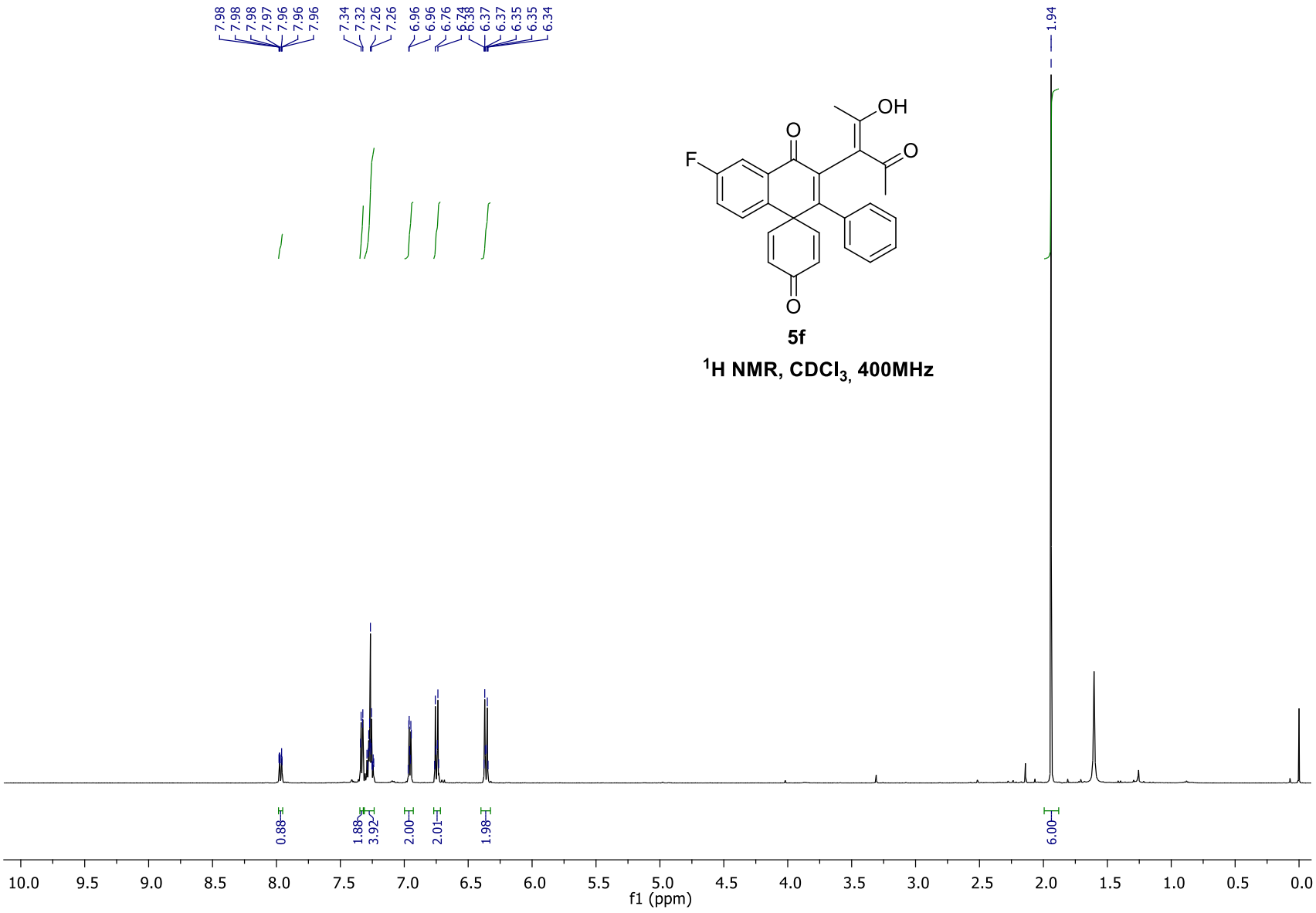
5e

^{13}C NMR, $CDCl_3$, 101MHz



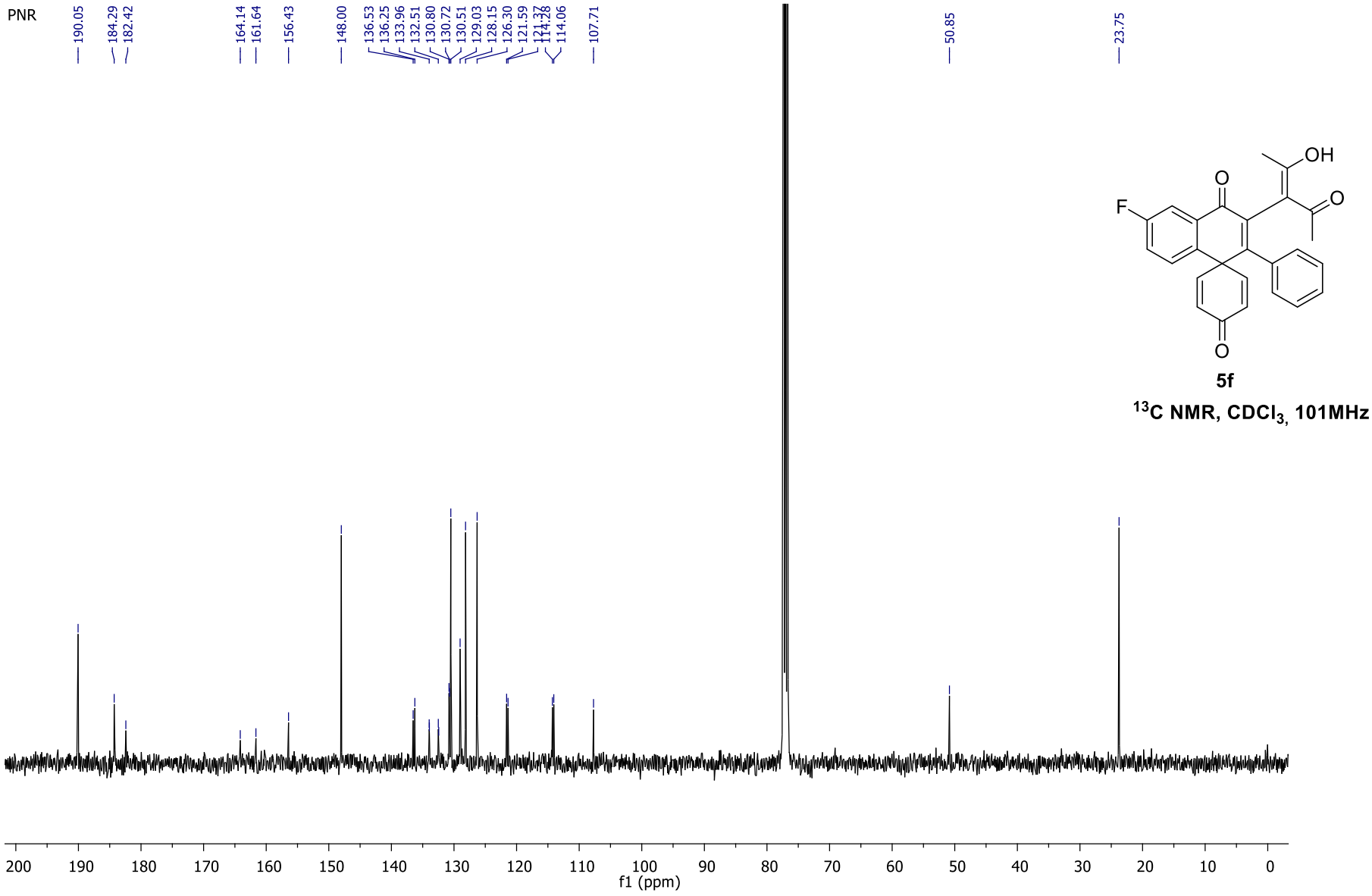
5e

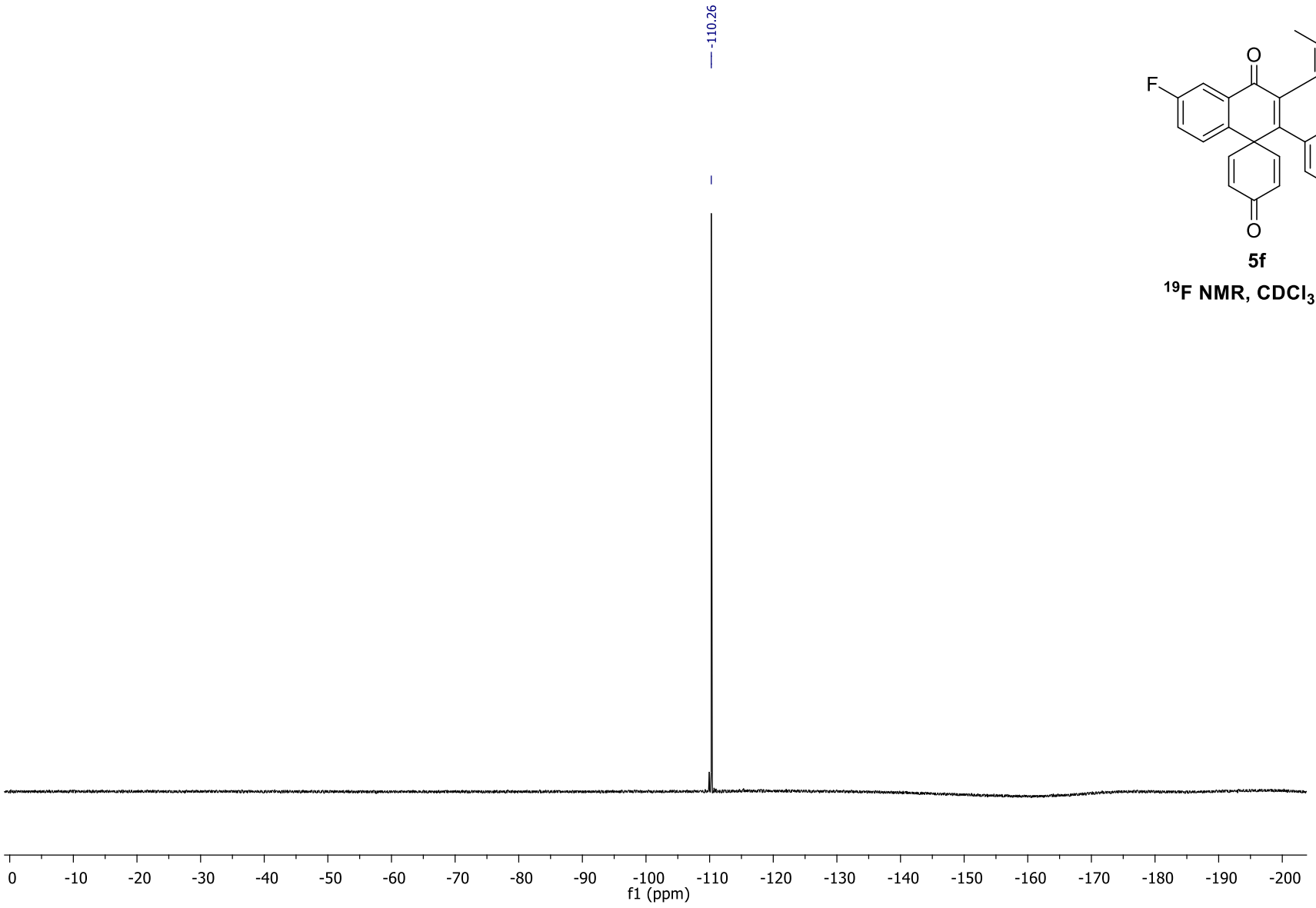
^{19}F NMR, $CDCl_3$, 376MHz



5f

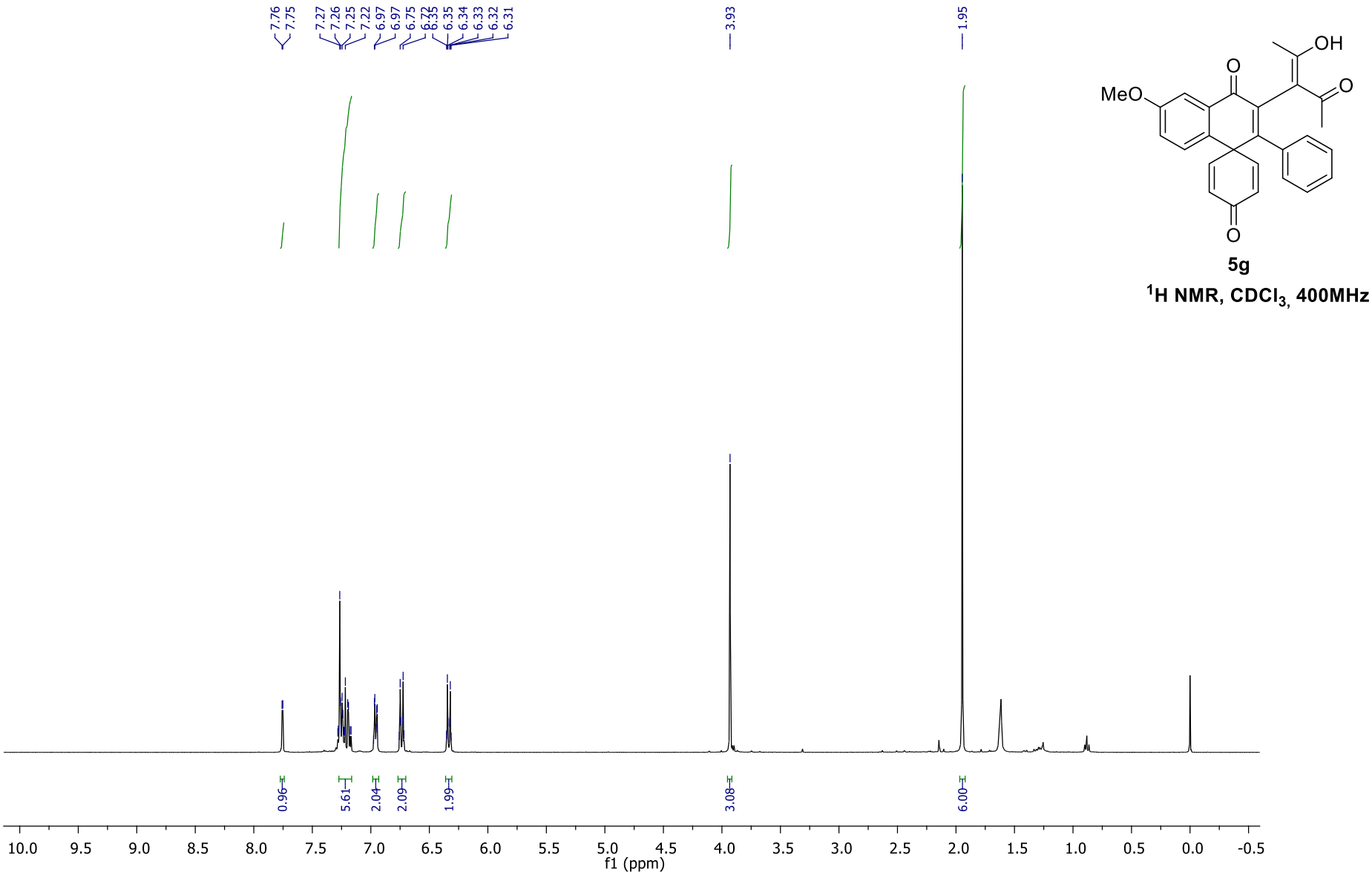
^{1}H NMR, $CDCl_3$, 400MHz


PNR
190.05
184.29
182.42
164.14
161.64
156.43
148.00
136.53
136.25
133.96
132.51
130.80
130.72
130.51
129.03
128.15
126.30
121.59
121.37
114.28
114.06
107.71
50.85
23.75
OH
O
O
F
O
5f
13C NMR, CDCl3, 101MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



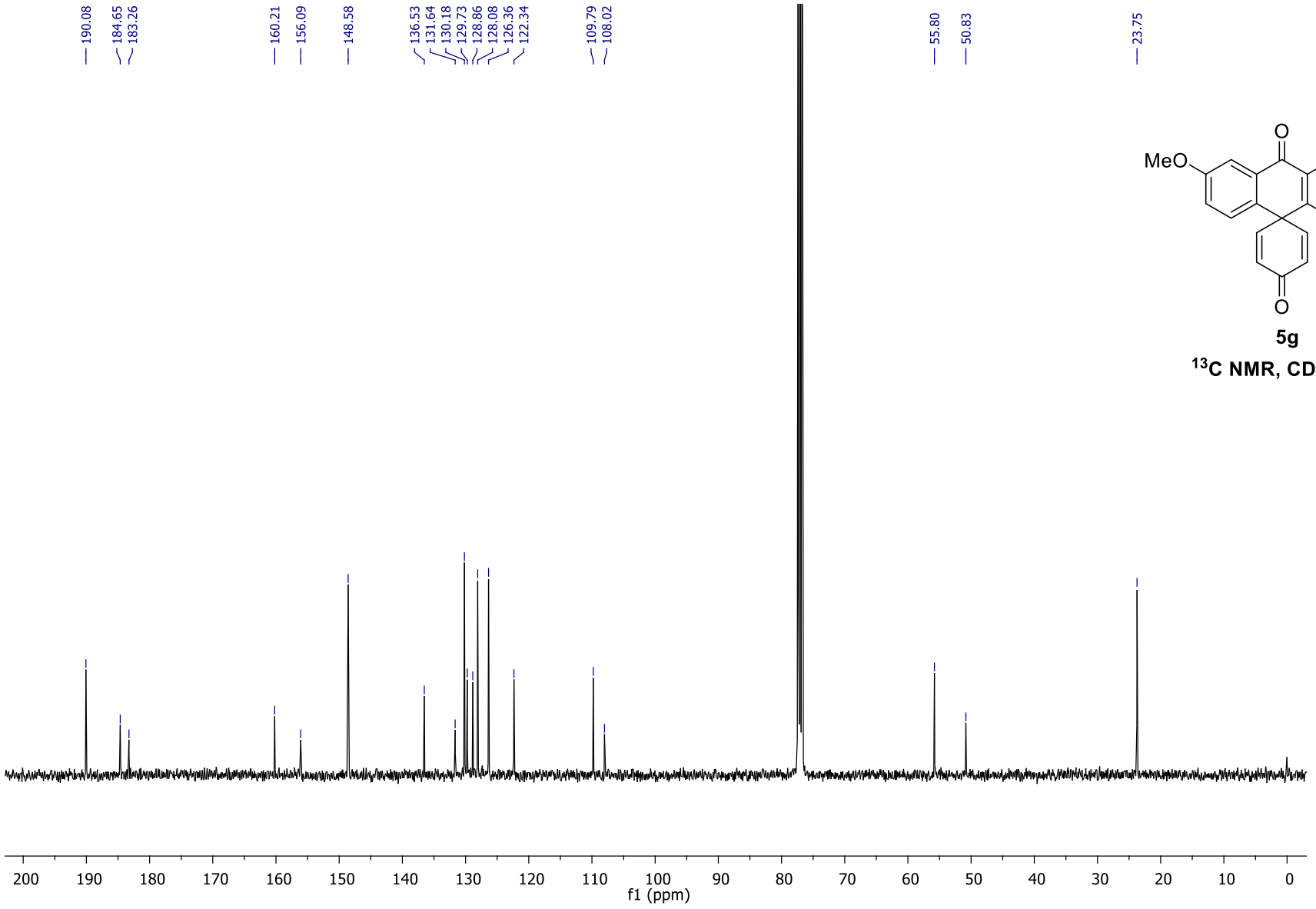
5f

^{19}F NMR, $CDCl_3$, 377MHz



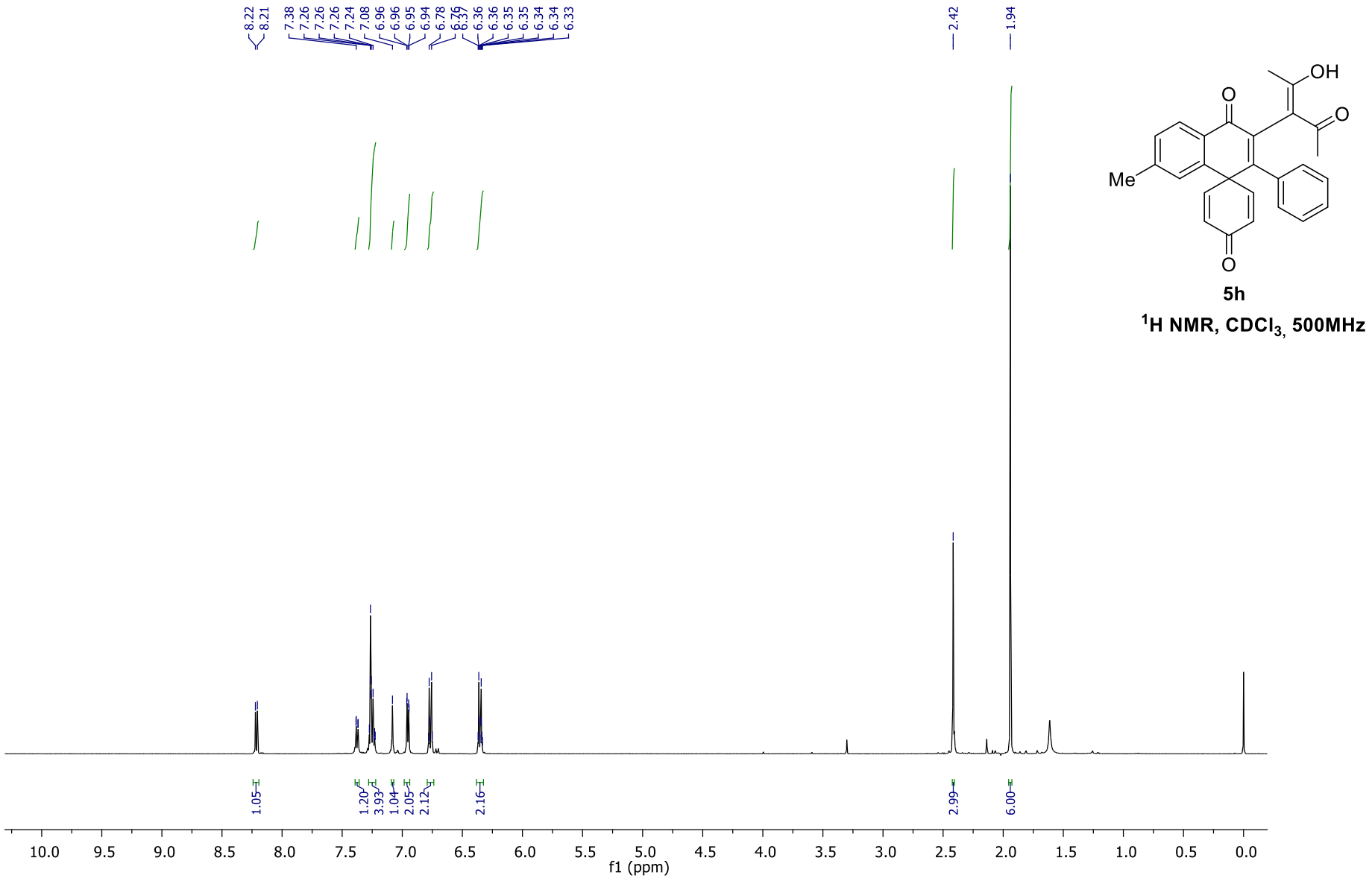
5g

^{1}H NMR, $CDCl_3$, 400MHz



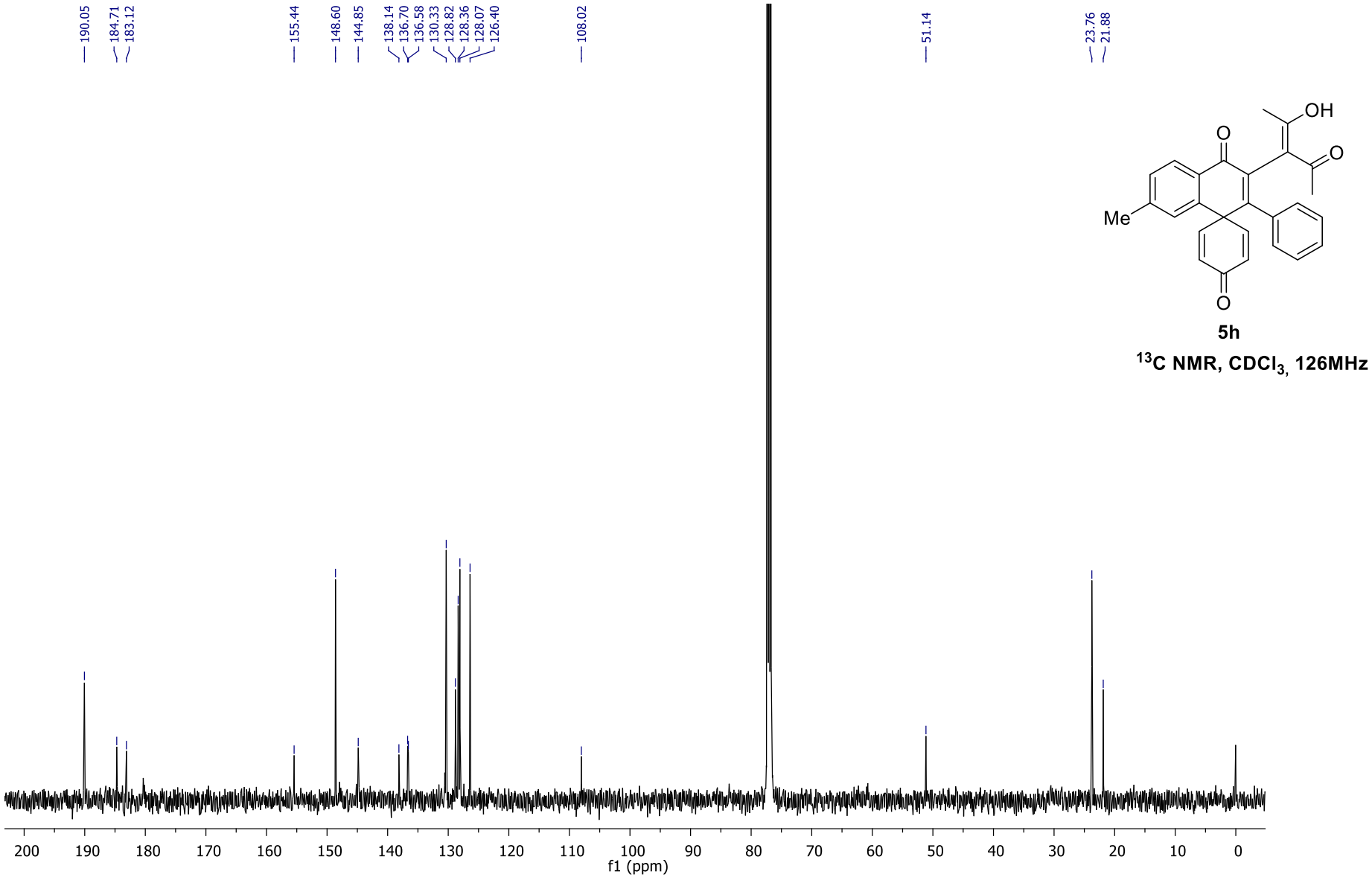
5g

^{13}C NMR, $CDCl_3$, 101MHz



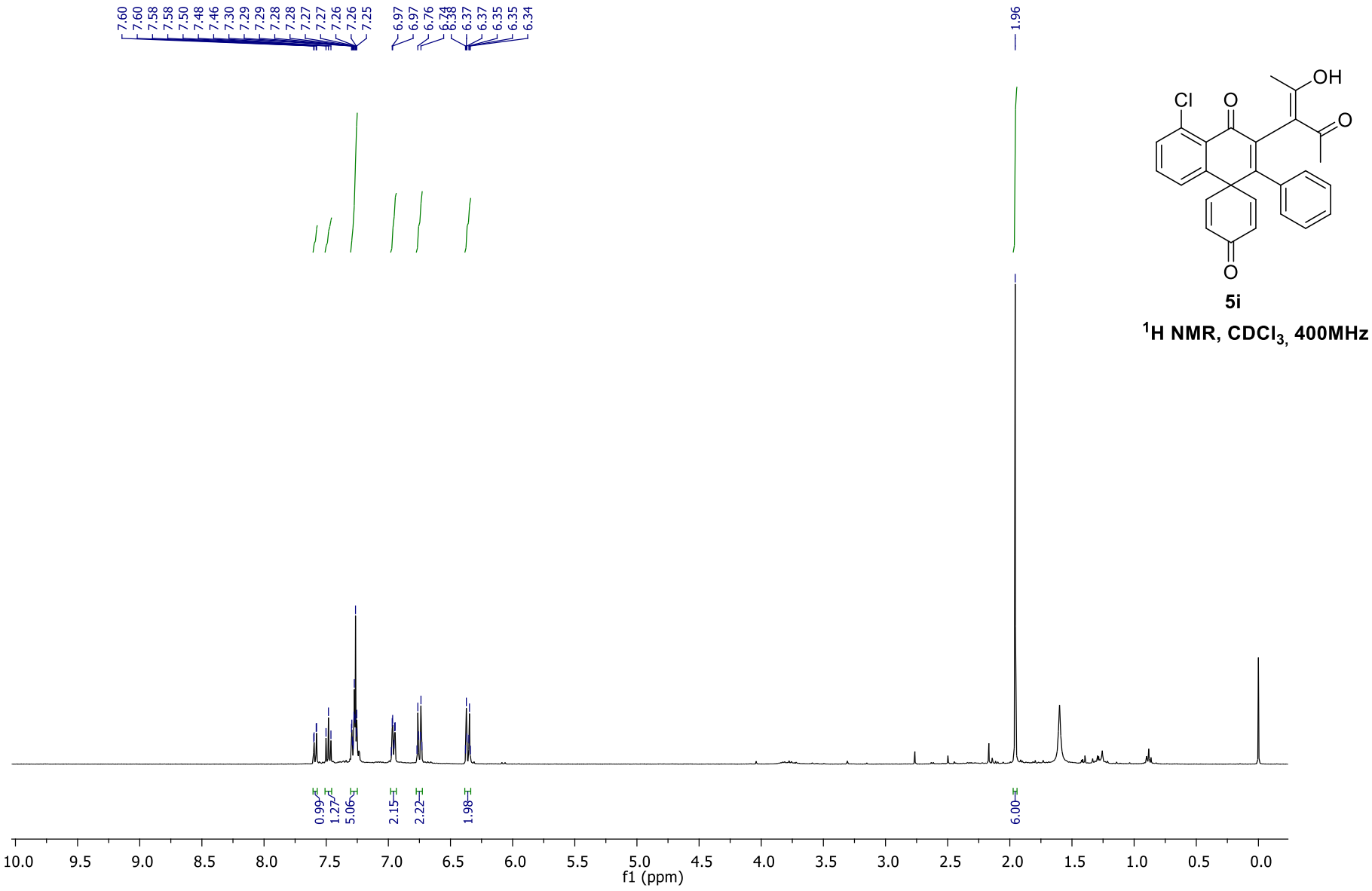
5h

^{1}H NMR, $CDCl_3$, 500MHz



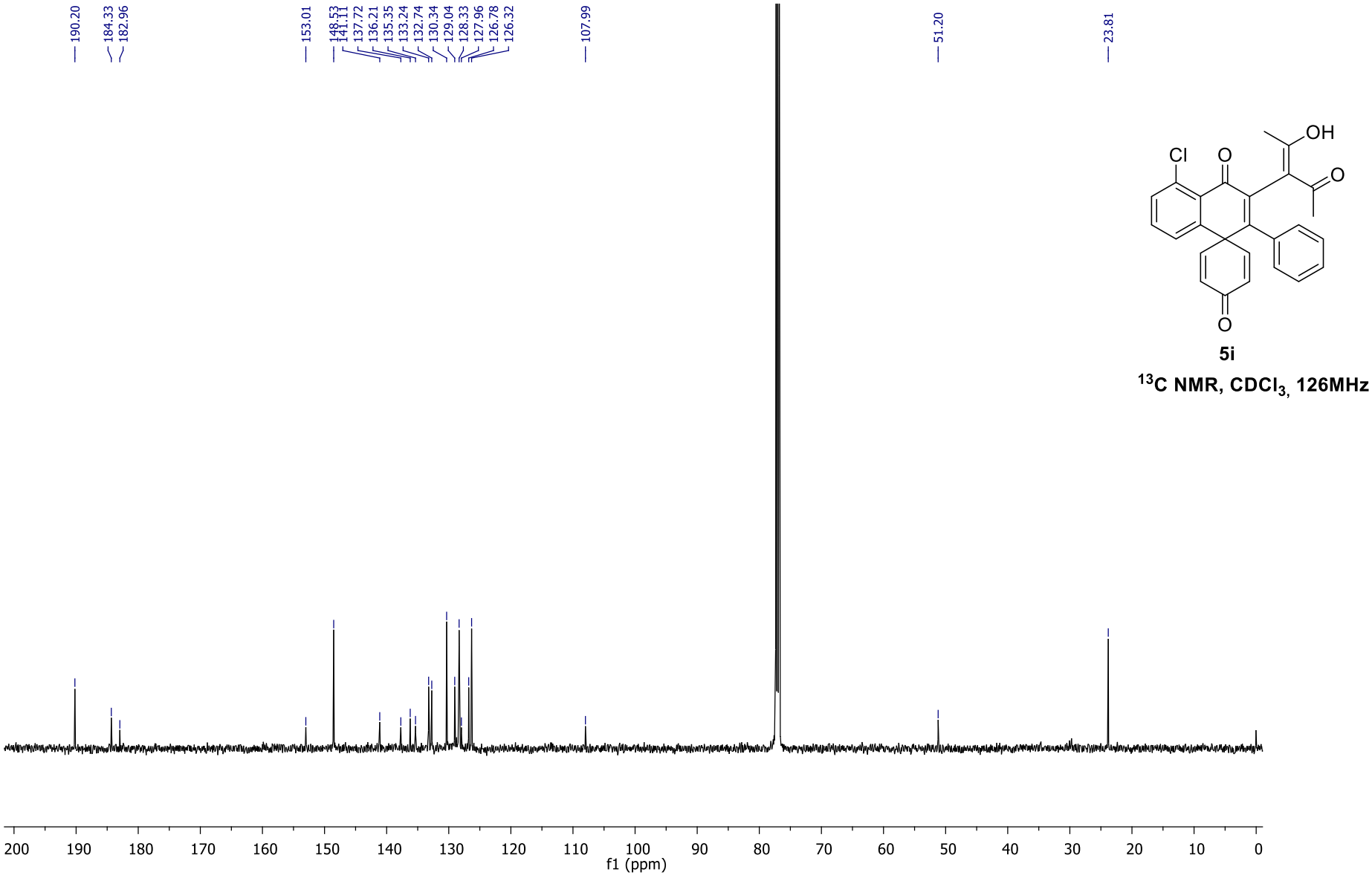
5h

^{13}C NMR, $CDCl_3$, 126MHz



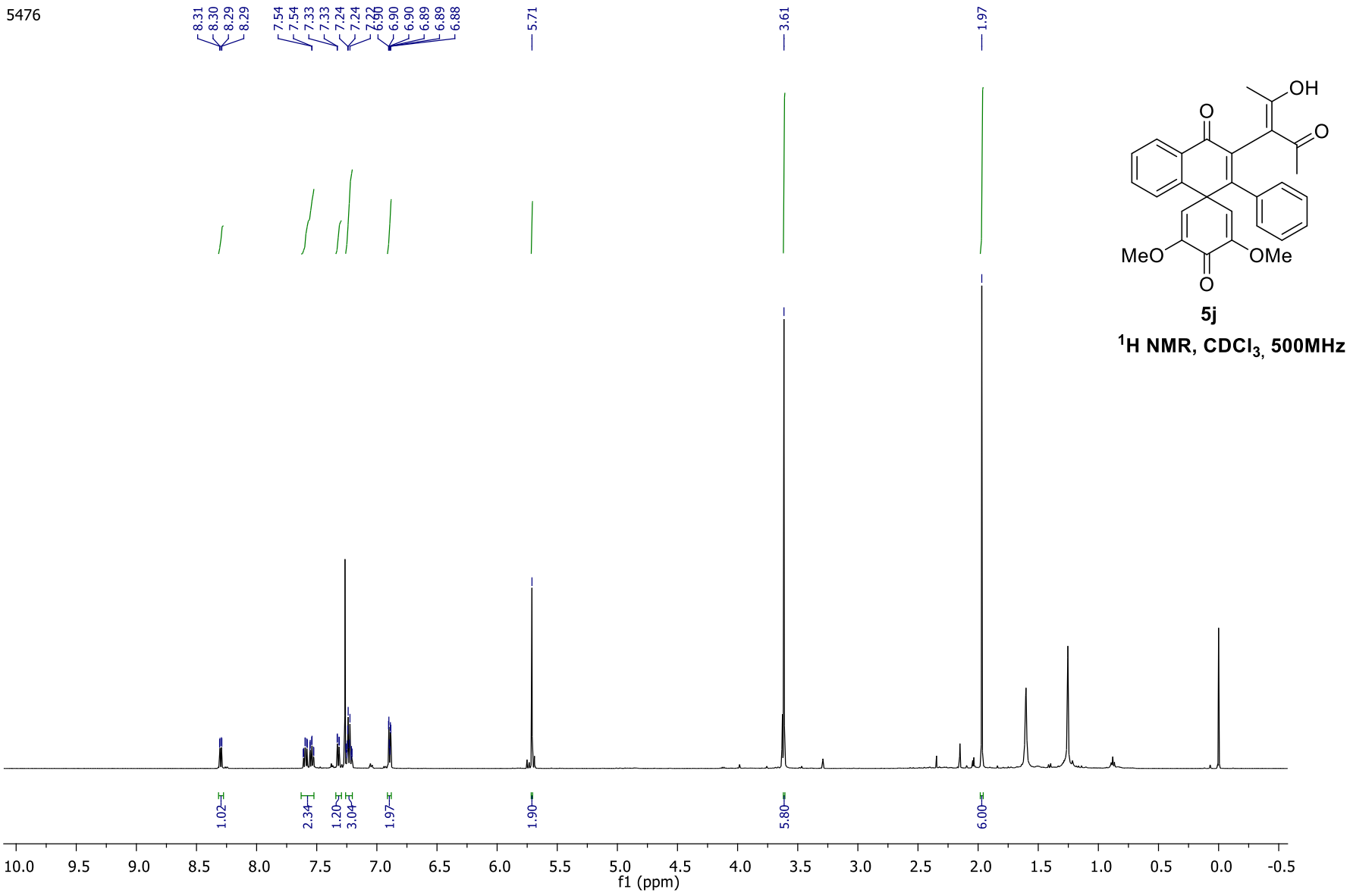
5i

^{1}H NMR, $CDCl_3$, 400MHz



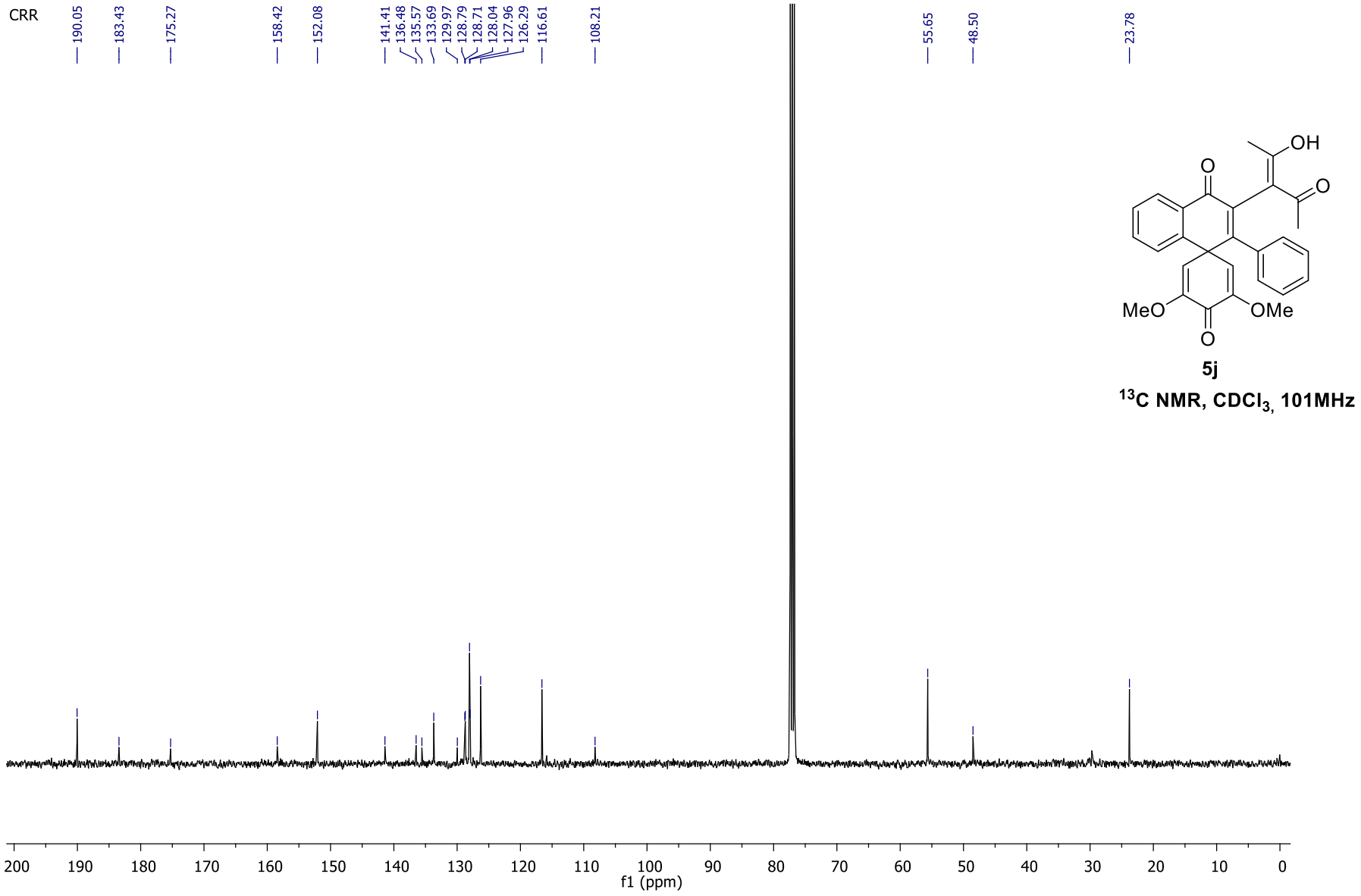
5i

^{13}C NMR, $CDCl_3$, 126MHz



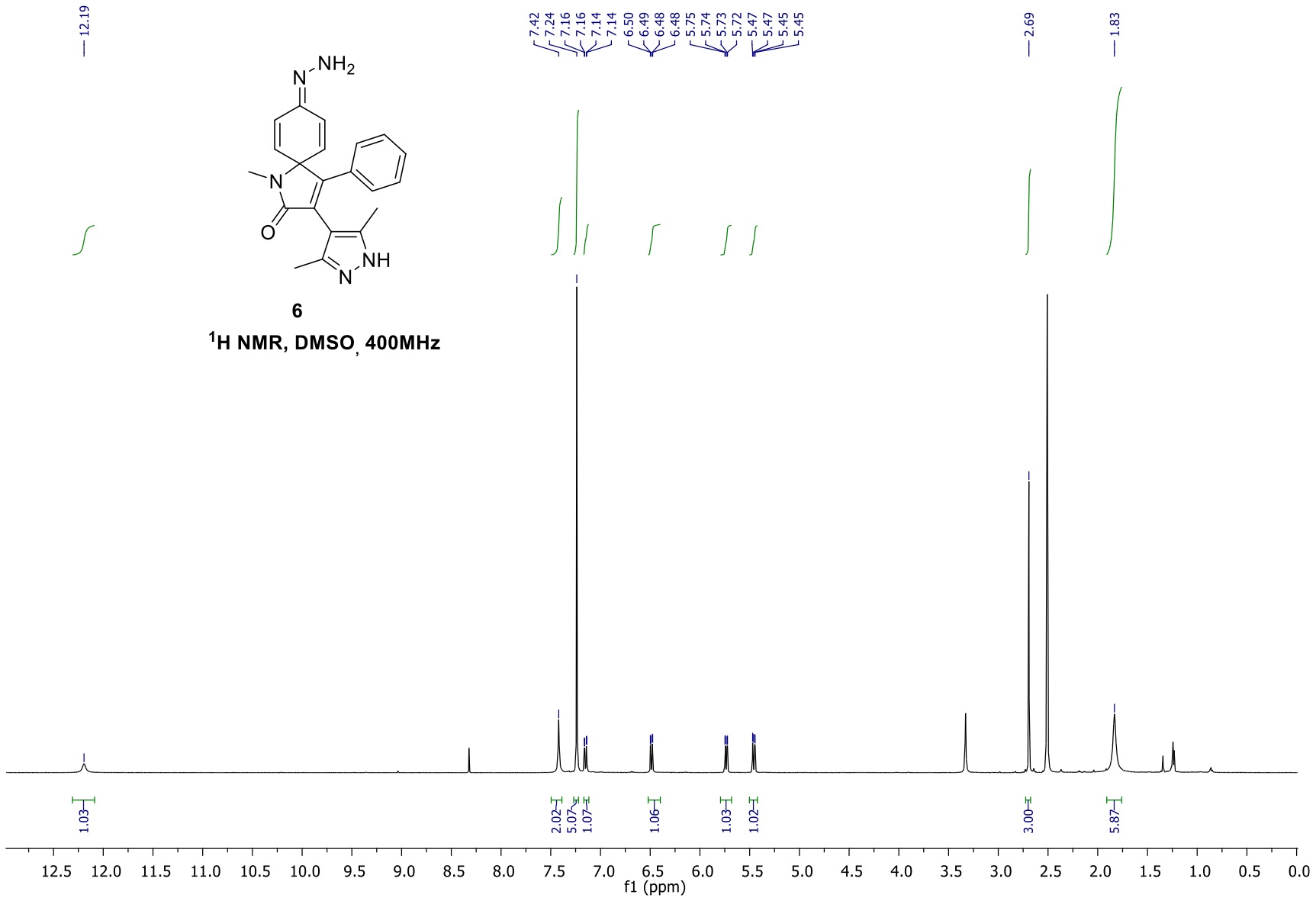
5j

^{1}H NMR, $CDCl_3$, 500MHz



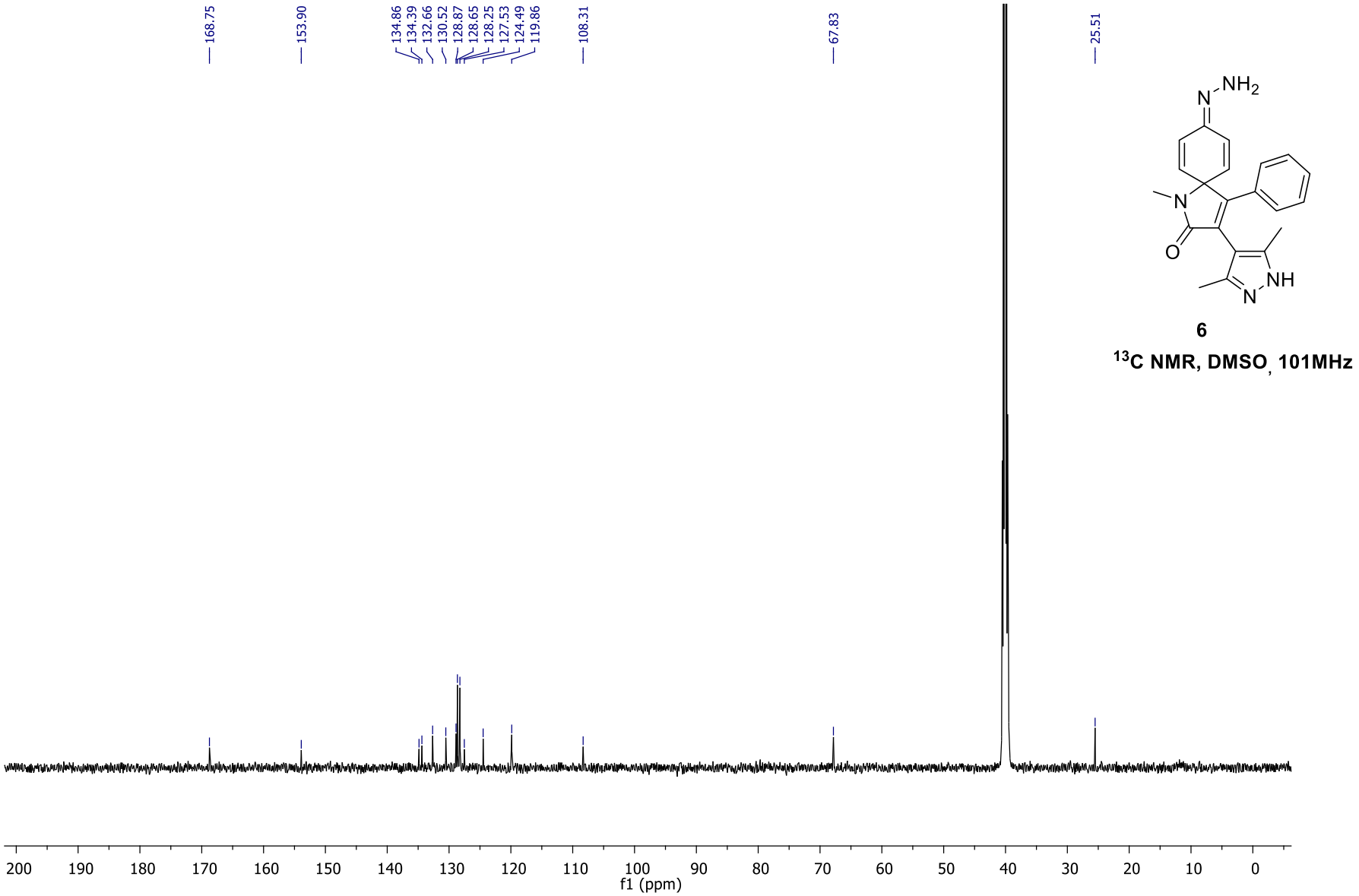
5j

^{13}C NMR, $CDCl_3$, 101MHz



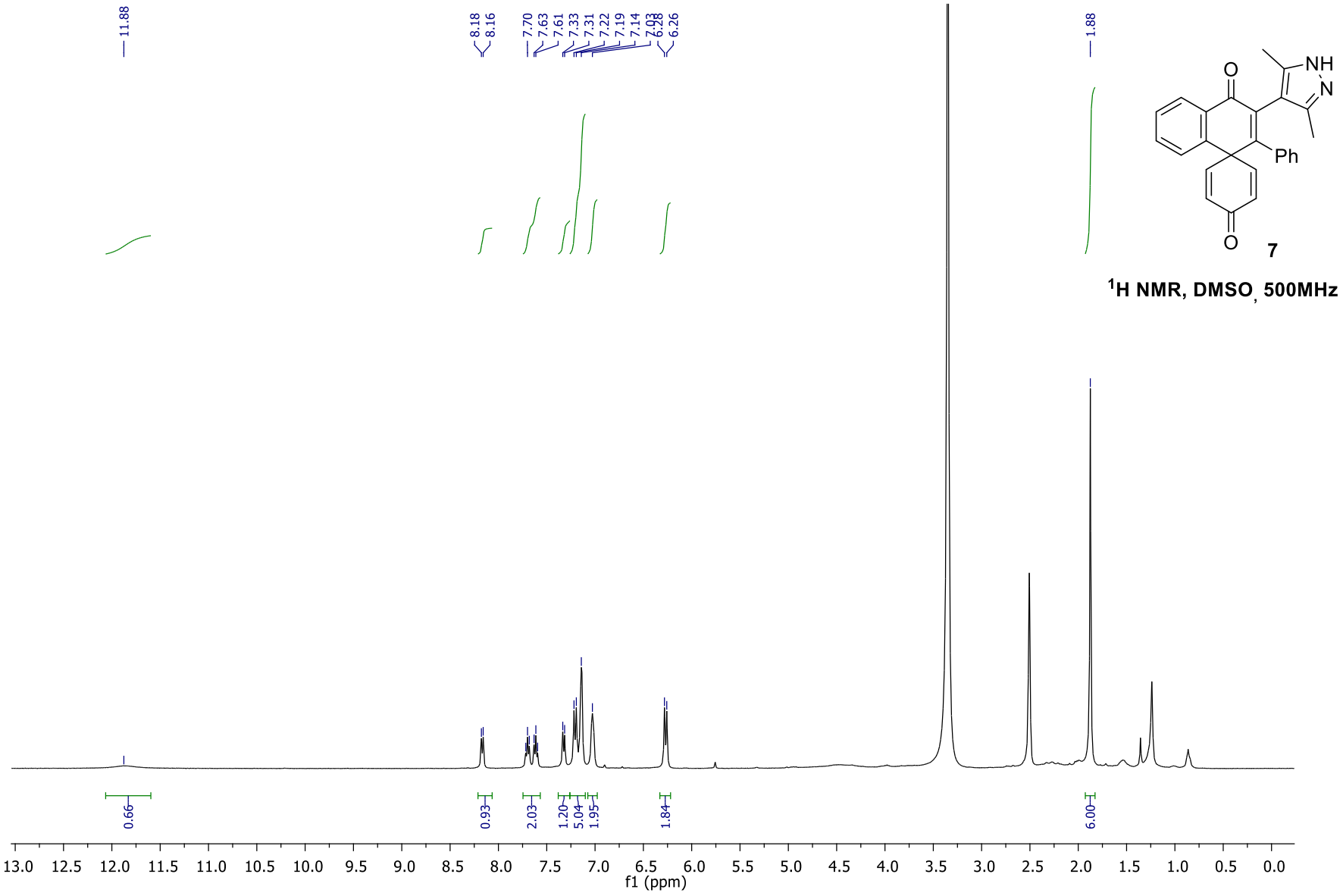
6

^{1}H NMR, DMSO, 400MHz

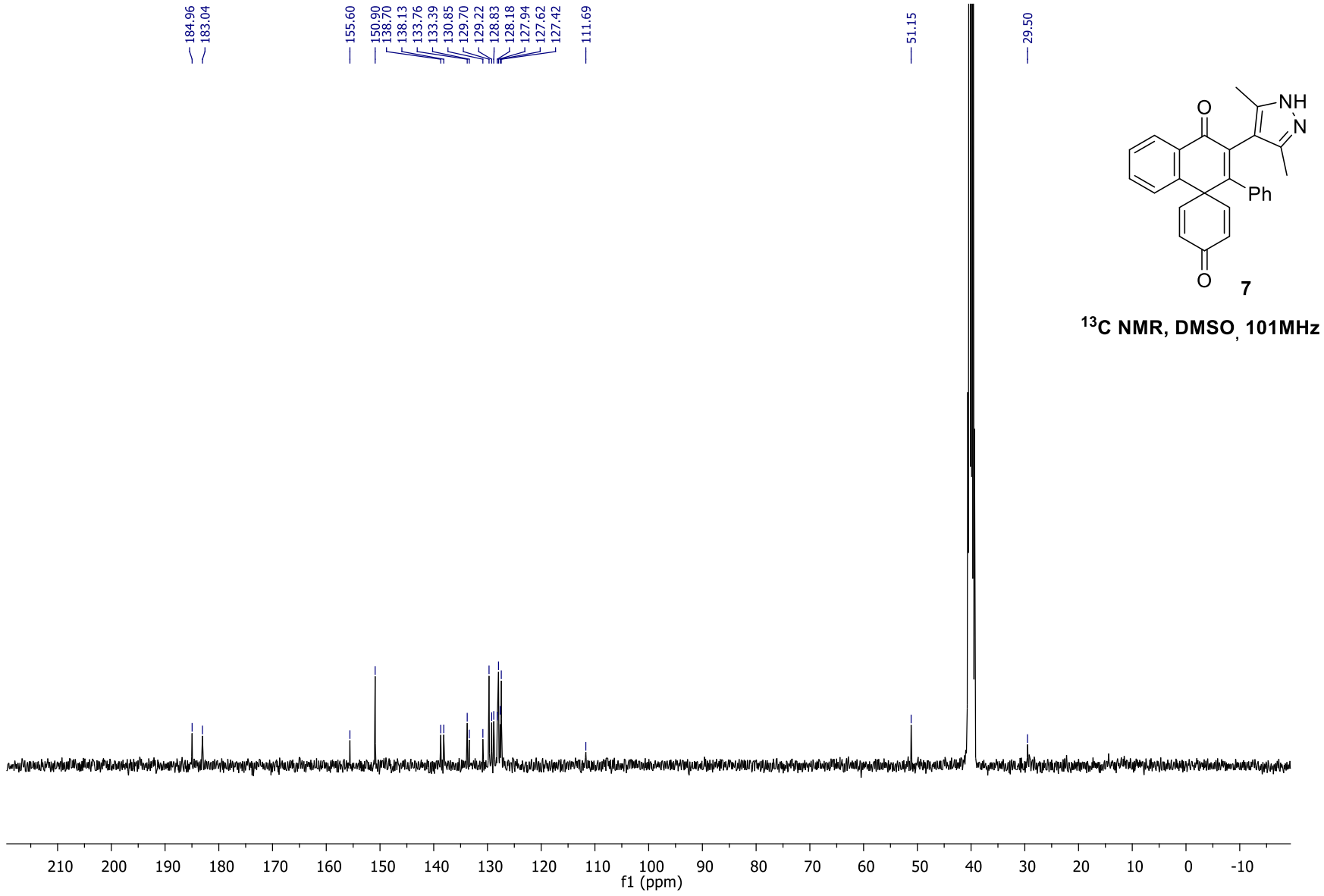


6

^{13}C NMR, DMSO, 101MHz



^{1}H NMR, DMSO, 500MHz


184.96
183.04
155.60
150.90
138.70
138.13
133.76
133.39
130.85
129.70
129.22
128.83
128.18
127.94
127.62
127.42
111.69
51.15
29.50
O
NH
N
Ph
O
7
13C NMR, DMSO, 101MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Created by: Shekar, Dr.Anubala

Created on: Feb 11, 2022

Item name: HRMS Elemental composition Feb 11, 2022 17:38:28 India Standard Time

Created time: 17:42:55 India Standard Time

Item name: CRR-255

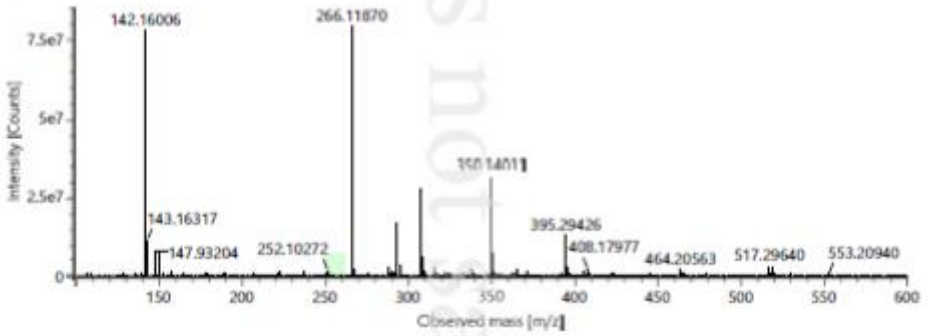
Item name: CRR-255, Sample position: 1:A,1, Replicate number: 1

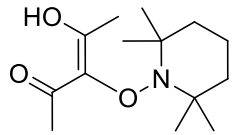
-	Component name	Observed neutral mass (Da)	Neutral mass (Da)	Observed m/z	Mass error (ppm)	Adducts
1	C14H25NO3	255.2568	255.18344	256.2641	286.5	+H

Component name: C14H25NO3

Item name: CRR-255
Item description:

Channel name: Low energy : Time 0.3112 +/- 0.0646 minutes





TEMPO-diketone adduct, **X**
HRMS found for $C_{14}H_{26}NO_3$:256.2641

Created by: Shekar, Dr.Anubala

Created on: Feb 10, 2022

Item name: HRMS Elemental composition Feb 10, 2022 12:08:23 India Standard Time

Created time: 12:12:56 India Standard Time

Item name: CRR-351

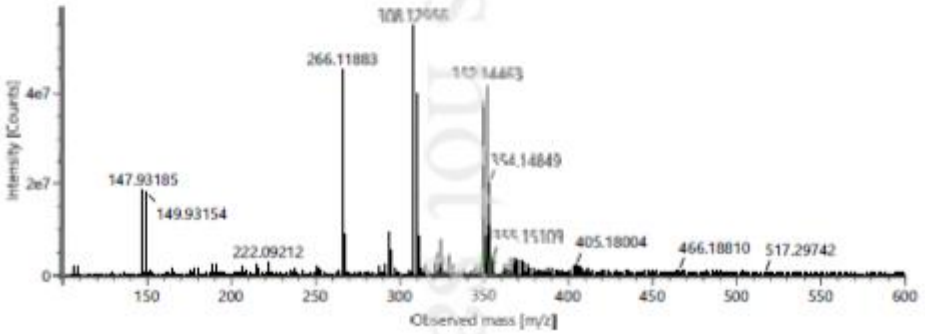
Item name: CRR-351, Sample position: 1:A1, Replicate number: 1

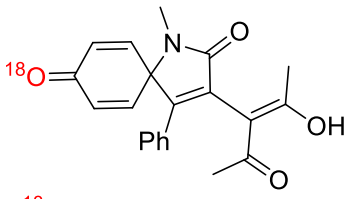
-	Component name	Observed neutral mass (Da)	Neutral mass (Da)	Observed m/z	Mass error (ppm)	Adducts
1	C21H19NO3[18O]	351.3848	351.13565	[illegible]	707.6	+H

Component name: C21H19NO3[18O]

Item name: CRR-351
Item description:

Channel name: Low energy : Time 0.3135 +/- 0.0581 minutes





^{18}O-**3a**, 89%

HRMS found for $C_{21}H_{20}NO_3{}^{18}O$: 352.3921